An Investigation into the Production of UHMWPE Fibres and Coatings for Protective Apparel

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Abstract

The primary aim of this research was to identify a novel process for the manufacturing of UHMWPE fibres and coating. Due to the high molecular weight of UHMWPE, it cannot be converted into fibres by standard extrusion processes it must be firstly dissolved in hydrocarbon solvents such as decalin, kerosene etc, which are unsustainable and potential hazards (to environment and human), then extruded to form a gel fibre. Following the extrusion process the solvent must be removed which involves the use of a secondary solvent e.g. n-hexane, toluene etc. which themselves are potentially hazardous.

Research revealed that terpene, a waste product of the orange juice industry was suitable substitute for the currently used solvents. Gel produced as a mixture of UHMWPE and terpene was successfully converted into fibres and fabric coatings. However, the ram process was initially found to be problematic, which was due to the presence of entanglement of the polymer chains. This was resolved by applying acoustic energy to the gel, which optimised the chain alignments thus reducing entanglement and allowing a consistent fibre to be ram extruded.

The terpene based extrusion process designed in this research eliminated the solvent removal stage, which eliminated the use of secondary solvent thus eliminating the hazards and cost associated with it. Since the process does not involve a separate solvent removal stage, it has the potential of reducing the processing cost.

The terpene also allowed a consistent UHMWPE coating to be applied to the cotton fabric. The coated fabrics showed a good resistance to highly concentrated acids, indicating the potential application of such coatings as protective apparel in the areas involving concentrated acid e.g. liquid acid battery, fertilizer industry, iron and steel making industries where acids are widely used. The coating process developed in this research has expanded the use of UHMWPE beyond the current possibilities.

DEDICATION

To my parents and my motherland

ACKNOLEDGEMENT

I would like to thank Dr A F Fotheringham and Dr Robert L Reuben for their advice and guidance throughout this work. Thanks also due to all technicians working in Scottish Borders Campus (SBC) specially James Mcvee and Roger Spark.

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Chapter 1 **Introduction**

1.1 Background

The market for high strength fibres and coatings is one of the fastest growing in the performance apparel segment i.e. sportswear, body armour, cut resistant, fire resistant, chemical resistant etc. After the September 11, 2001 attacks, the demand for high strength fibres dramatically increased [1]. Increased demand of such fibres resulted in the installation of new production lines by major manufacturers [2]. The increasing use of such fibres in diverse applications such as cut resistance, bullet resistance, heat resistance, motorcycle wear, protective gloves sportswear etc is partly responsible for the increased demand.

Glass fibres were the first non-metallic fibres manufactured which found applications in fibre composites for use in aircraft, boats, sports equipments etc. Later developments included carbon fibres which were stronger, stiffer and lighter. Initially, polymer fibres could not reach strength levels comparable to glass and carbon fibres. However, the development of solvent-based spinning technology made production of ultra strong fibres possible. These fibres could be divided in to two groups: one with rigid rod molecules e.g. Aramid and PBO, and the other group with very long polymer chains e.g. UHMWPE.

1.1.1 Fibres

The advantages of high performance fibres on the conventional materials are significant. The ability of these fibres to provide high strength at very low weight is one of the most important consideration and brought about a revolution in the aeronautical industry, since lower weight meant lower fuel consumption [3]. The high strength fibres made lightweight flexible bulletproof vests possible, the ability of these fibres to resist high temperature made fire protective clothing possible and chemical resistance is another important feature of these fibres.

UHMWPE is one of the strongest fibres currently available and is rapidly gaining acceptance in a variety of applications [4]. The strength of UHMWPE is 35% more than the aramid fibres on a weight to weight bases and it has the lowest density amongst the high strength fibres. The UHMWPE offers twice the modulus of aramid

fibres. It is about 2/3 less dense than the high modulus aramids, and about half that of high modulus carbon fibre [5]. UHMWPE abrasion resistance is better than aramids and carbon fibres. The resistance to UV radiation and highly alkaline and acidic chemicals of UHMWPE is better than aramids, PBO (Polyphenylene Benzobisoxazole) and LCP (Liquid Crystal polymer) [6]. Due to very good physical and chemical properties, UHMWPE is widely used in applications such as bullet proof vests, load carrying ropes, cut resistant apparel, fishing lines, fishing nets, medical inserts etc. The ability of UHMWPE to provide same strength as aramid at 35% less weight is advantageous when used for body armour where weight plays a vital role. Due to inert nature of the UHMWPE these fibres resists host of chemicals exposed to law enforcement agencies and also faced by military personnel on the battlefield [7]. UHMWPE fibres are also used in unidirectional cross-plied nonwoven composites introduced by Honeywell. These unidirectional cross-plied nonwoven composites enable more fibres to engage the projectile and disperse the energy 360^{o}. This technology enabled a lighter more comfortable vest practical. UHMWPE fibres are also used in moulded armour products where high pressure is utilised to consolidate the fibre packing density in the moulded product. Due to very high fibre density and viscoelastic properties of UHMWPE these moulded products can stop the projectiles at almost 50% lesser weight than the previously moulded armour products [7]. These fibres are widely used in the armoured personnel carriers (APVs), Humvees and mine protected vehicles. Helicopters and aircraft are also protected from the emerging threats by utilising the light weight armours made from UHMWPE fibres. At sea the light weight of UHMWPE enables the boats such as inceptors, fast petrol, and offshore patrol vessel to be protected from the threats without compromising their performance. Cut resistant T-shirts are another area where UHMWPE fibres are widely utilised to protect correctional officers and law enforcement officers from the threats of cutting and slashing objects. The cut resistance gloves made from UHMWPE are used in meat industry to protect the workers from the knife cuts. The cargo boxes and nets made up of UHMWPE not only provide a stronger alternative to the traditional options they are also 50% lighter, which significantly reduces the fuel consumption. UHMWPE load carrying ropes are easier and safer to work with due to their light weight which is 80% lighter than the metal ropes, it also avoids the risk of fatal injuries in case of rope snap. Due to low density, UHMWPE floats on water and combined with its cut resistance makes it an ideal material for fishing net which resists fish bite cuts. Due to its lower weight it also reduces the fuel consumption in carrying the nets during fishing hence

reduces the carbon print. Sailing is another area where the very high strength combined with very low weight and high resistance to natural degrading agents made UHMWPE a material of choice for sail cloths. The Sails made up of UHMWPE does not absorb water and retains their shape, it lasts longer despite of being less bulky than the traditional sail cloths. UHMWPE fibres are used in a wide variety of sportswear such as cycle gear, ice hockey and motor cycle gear to protect the wearer from cuts, abrasion and tears. Medical inserts is another area of application e.g. high strength sutures, ligament repair, arthroscopic procedures, motion-preserving spinal applications etc. where UHMWPE is widely used because of its inertness which avoids rejection problems.

Gel spinning is the widely used process for the production of UHMWPE fibres. The process involves the dissolution of UHMWPE powder in petrochemical solvents e.g. paraffin, decalin, dodecane, kerosene, p-xylene, diethyl ether, n-pentane, methylene chloride, n-hexane, toulene [8-10]. The polymer solution is then extruded to form fibres. The fibres extruded are in the form of gel containing both polymer and solvent. To achieve dried fibres the solvent is removed by utilising another volatile hydrocarbon solvent which replaces the spinning solvent in the gel fibre. The volatile hydrocarbon solvent is then removed by evaporation to achieve dry fibres.

1.1.2 Coatings

Coating is a widely used process to improve the surface properties of the fabrics. The coated fabrics are extensively use in chemical resistant apparels. The hot air balloons are another area of application. A new emerging market for these fabrics is the high performance tents where the coated fabrics are used to protect the occupants from the extreme weather. The wear resistant coated fabrics are widely used as load carrying ropes. The water proof coated fabrics are widely used in sports equipments and high performance protective work wear. In agriculture industry coatings are used in shade material, irrigation systems, pond liners, hoses, bags, seed/crop covers, fencing, bulk containers etc. In construction industry coated fabrics are used in safety fencing, wind covers, concrete curing, safety vests, hoses, conveyer belts, truck covers, drainage ditches, architectural structures etc. In the clothing industry coatings are widely used in shoe uppers and linings, artificial leathers, rain wears, garment linings, backing stiffeners, water replants, stain repellents etc.

The fabrics are being coated with variety of polymers e.g. polyurethane, polyvinyl chloride etc. depending on the performance requirement. UHMWPE have very good chemical resistance combined with its very high strength and wear resistance can revolutionize the coating industry. The coatings can expand the use of UHMWPE beyond the current possibilities. The chemical resistance of the UHMWPE is extraordinary due to its inert nature it can with stand concentrated acids and alkalies. Its ability to resist chemicals is advantageous in variety of industrial, military and leisure applications. The other area of application can be sportswear where the wear resistant, UV resistant, weather resistant properties of UHMWPE are advantageous.

1.2 Issues

The process of producing UHMWPE fibres involves petrochemicals. Since all of the chemicals presently in use to produce UHMWPE fibres are derived from petroleum, they are not sustainable. There are limited supplies of petroleum resources. These resources must be utilised wisely and should be avoided wherever possible. Since the demand of the high performance fibres is increasing day by day, the utilisation of these unsustainable chemicals will lead to the depletion of the oil reserves.

The solvents used in the production of UHMWPE are a known hazard to environment. They are toxic to the aquatic life due to their high mobility in soil they carry the risk to contaminate the ground water. Since these chemicals are derived from crude oil, they are not biodegradable. Due to their inability to biodegrade, these chemicals cannot be disposed easily.

The health hazards of the petrochemicals used in production of UHMWPE fibres are a very serious concern. These chemicals are known to cause saviour illness e.g. cancer, nephropathy, lung damage, central nervous system damage, kidney damage, liver damage etc.

In the production process of UHMWPE the extraction of the spinning solvent is a stage where spinning solvent is removed by utilising other petrochemicals these petrochemicals carry the same problems mentioned above. Additionally the sole purpose of this stage is the removal of the spinning solvent. The environmental effects and health hazards of this stage are enormous while it also adds to the cost of the process.

UHMWPE drives its strength from the very long polymer chains. In the absence of other inter-polymer forces, van der Waals' forces are the prominent forces of attraction. For van der Waals' forces to be effective the polymer chains needs to be aligned to each other. Since UHMWPE contains very long chains which give rise to the entanglements. These entanglements resists the alignment of the polymers hence results in the weaker fibres.

Extensive research had been reported in the literature on the process of producing UHMWPE fibres. However, there is no mention of the UHMWPE coatings. Unlike other coating materials, the UHMWPE coating is not very straightforward. The problem associated with coating is its very high viscosity and its solutions instability at room temperature. The complete absence of data regarding UHMWPE poses many challenges. First of them is the preparation of the polymer solutions. The second challenge is to find out the optimum concentration of the polymer for coating solution. The third problem is the instability of the polymer solution at room temperature as it is well known the polymer solution of UHMWPE undergoes phase separation below a certain temperature. The fourth problem is to identify the process for application of the coating solution.

1.3 Expected Outcomes

A process will be developed which will utilise a sustainable solvent for the production of UHMWPE. This solvent will completely replace the petrochemical solvents used in the present process, which are derived from the crude oil. The new sustainable solvent will reduce the pressure on the oil reserves. Since the oil reserves are very limited the use of this sustainable solvent will also make sure the process would not be affected by the cost of the petrochemical resulted by the depletion of the oil reserves in future.

The solvent would also be environmentally friendly, the presently used petrochemicals are not biodegradable, due to which they pose serious environmental risks to aquatic life and contamination of the ground water. The biodegradable nature of the alternative solvent will result in an environmentally friendly process. Hence, it will eliminate the cost associated with the safe disposal of the used petrochemical solvents.

The new suitable solvent would also be safer to the human. The present solvents are hazardous to human and can cause a variety of short term and long illnesses e.g. cancer, nephropathy, lung damage, central nervous system damage, kidney damage, liver damage etc. It would result in better working conditions for the workers involve in the production process that will result in the increased efficiency of the workers.

The solvent extraction stage would be eliminated. In the present process, the solvent extraction is carried out by utilising more volatile petrochemical, which has their own issues similar to spinning solvents i.e. sustainability, environmental hazards and health hazards. The elimination of this stage will result in the elimination of the secondary solvent hence, improving the sustainability of the process. It will also reduce the environmental and health hazards. The elimination of this stage will eliminate the cost associated with the chemicals used in the extraction. Due to elimination of the whole extraction stage the cost associated with the running of this stage will be eliminated resulting in a cheaper process.

The UHMWPE fibres depend primarily on the alignment of the polymer chains for their strength. Since the UHMWPE consists of very long polymer chains which give rise to entanglements, these entanglements resists the alignment of the polymer chains which results in weaker fibres. The ultrasound treatment is expected to disentangle these chain entanglements resulting in more align and stronger fibres. This could lead to design a machine fitted with acoustic, which will improve the alignment of the polymers before the extrusion, opening a new avenue for research not only in UHMWPE extrusion but also in other polymers.

A process for the coating of UHMWPE on the cotton fabric will result in a chemical resistant fabric having the comfort of cotton while providing the protection of UHMWPE. The coating of the UHMWPE is an unexplored territory there is no mention of the UHMWPE coating in literature. The development of the coating process will open a new avenue for research for the applications in variety of fields e.g. motorcycle wear, chemical resistant apparel, sportswear, high performance work wear, law enforcement vest, sports equipments etc.

1.4 Objectives of the Thesis

The fundamental goals of this thesis are to find first an alternative sustainable, environmentally friendly and user friendly solvent to petrochemicals used in the production of the UHMWPE fibres. The second goal is to develop a process which will enable the coating of UHMWPE which will expand the use of UHWMPE beyond the current possibilities. In order to achieve these overall goals, the following objectives are set for this study:

- To identify a sustainable, environmentally friendly and user friendly solvent for the production of UHMWPE
- To identify a process which eliminates the use of extraction solvents
- To develop a process which will eliminate the solvent extraction stage
- To investigate the effect of different factors through systematic experimental approach on the strength of the fibres
- To investigate the effect of ultrasounds for the improvement of polymer chain alignments
- To identify, through preliminary study, the main parameters and conditions which affect the coating process
- To develop a coating method based on the preliminary study, which will enable the coating of UHMWPE

1.5 Structure of the Thesis

This thesis comprises seven chapters. The present chapter provides a background of the topic, methodology, expected outcomes, objectives of the thesis and structure of the thesis.

Chapter 2 reviews the structure of polymers in general and UHMWPE in particular. It reviews the technology for the production of UHMWPE fibres. The review also covers the problems associated with existent fibre production process. The blends of UHMWPE have also been reviewed. It also reviews the role of ultrasonic in polymer chemistry. The coating processes have also been reviewed. A number of potential natural alternative solvents are also discussed.

Chapter 3 gives the details of the methodology adopted. It gives information about instruments and the materials that were used for the production and analysis of fibres and fabric coatings.

Chapter 4 contains experimental work carried out to find an environmentally friendly process for the production of UHMWPE. The blends of the UHMWPE with polypropylene and polyethylene are investigated. The natural oils are examined to find an environmentally friendly solvent for the production of UHMWPE fibres. Experimental design is implemented to find the factors, which influence the strength of the fibres while using the natural alternative solvent. The ultrasonic treatment is also examined for its effects on the orientation of the fibre.

Chapter 5 gives the details of the coating experiments conducted to achieve UHMWPE coating on cotton fabric. The chapter describes the development of a modified process to coat UHMWPE on cotton fabric. The resistance of the coated fabric against the sulphuric acid and nitric acid is being examined. The chapter also includes the comparison between the strength of coated and uncoated samples.

Chapter 6 contains the additional work carried out to integrate the fire retardant into the UHMWPE fibres. The process to produce fire retardant integrated fibres is explained. The effects of the different percentages of fire retardant on the fibre properties are also covered in this chapter.

Chapter 7 discusses the outcome of the experimental work. Different aspects of terpene process are being discussed comparing it with the traditional gel spinning process. The chapter includes the discussion on the coating process. It also includes the conclusion drawn from the present work and recommends the future work.

Chapter 2 **Literature Review**

2.1 Introduction

This chapter presents the literature review which provided the foundation for this research. The review includes a brief explanation of polymer chemistry followed by inter-polymer forces and intra-polymer forces. Fibre morphology and its effect on the fibres properties have been also discussed. The properties of UHMWPE compared to other polymers have been reviewed. This chapter also covers the different processes reported for the preparation of UHMWPE fibres. Different machines and chemicals reported for the preparation of UHMWPE fibres are discussed. Gel spinning which is the most widely reported process has been reviewed intensively. The review of gel spinning includes the extrusion techniques, solvents used, solvent extraction methods, polymer concentration, drawing and the environmental and health risks associated with it. The polymer blends in general and blends of UHMWPE in particular are also reviewed. The potential natural alternatives to the petrochemical solvents used in UHMWPE fibres preparations are also discussed. The role of ultrasonic energy in the polymer chemistry has also been reviewed. The last section reviews the factors which affects the coating process. It also reviews the different mechanism used to apply the coating onto the fabric.

2.2 Polymer

The basic unit of fibre is called polymer. Like other substances, fibres are made up of molecules and these molecules are called polymers. The word polymer is derived from the Latin word *poly* meaning many and *mer* meaning unit. A polymer consists of many small units called monomers also derived from the Latin word *mono* meaning one [11]. Polymers are extremely long molecules consisting of hundreds, thousands, or even millions of atoms joined. Polymers tend to be nonreactive. However, monomers are highly reactive. This behaviour is illustrated in the chemical process called polymerization in which monomers join end to end to form a nonreactive longer molecule referred to as a polymer [12]. In general, polymers are nonreactive but this does not prevent the degradation of polymers by chemicals. The length of the polymer is the most important factor in both natural and manmade fibres. Accurate measurement of the length of the polymer is difficult if not impossible while the degree of

polymerization gives the estimate of polymer length, which is also abbreviated to DP. Equation 2.1 shows a formula to calculate the degree of polymerization.

$$DP = \frac{average\ molecular\ weight\ of\ polymer}{molecular\ weight\ of\ the\ repeating\ unit\ in\ the\ polymer} \qquad (2.1)$$

Types of polymer:

There are two main types of polymers

1) Homopolymer
2) Copolymer

2.2.1 Homopolymer

The polymers which are polymerised from same or one kind of monomers are called homopolymers [13]. Examples of such polymers include nylon 6, nylon 11, polyethylene, polypropylene, polyacrylic and modacrylic. Figure 2.1 shows a polyethylene polymer chain, an example of homopolymer where whole polymer is made up of one type of monomer i.e. polyethylene.

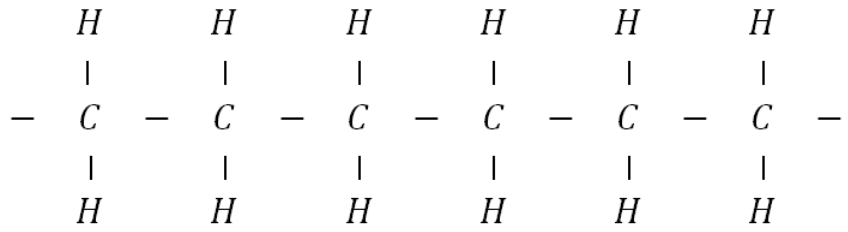

Figure 2.1 Extended structure formula of polyethylene polymer

2.2.2 Copolymer

Copolymers contain more than one type of monomer [13]. These monomers could be in alternating sequence that are called alternating copolymers or arranged in segments or blocks referred to as block copolymers. Additionally there are some copolymers in which the monomers are randomly arranged and some with monomers attached as branches (side chains) to the main polymer chain referred to as random copolymers and graft copolymers respectively [11]. Nylon 6.6 is copolymer as shown

in Figure 2.2 containing two types of monomers i.e. hexamethylene diamine and adipic acid.

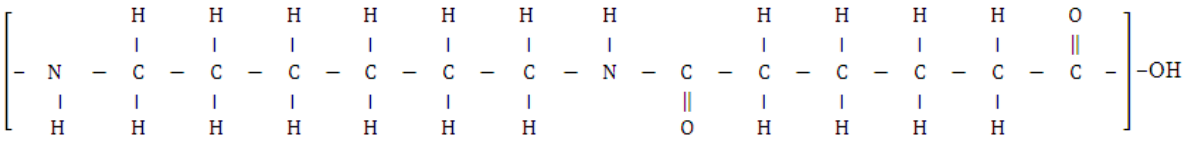

Figure 2.2 Nylon 6,6: an example of a copolymer

2.3 Intra-polymer Forces

A polymer is equivalent to a molecule capable of existing on its own while maintaining its properties. Intra-polymer forces are referred to as the forces or bonds holding the atoms together in a polymer. Most of the man made polymers are derived from organic compounds and therefore predominantly contain hydrogen and carbon atoms hence covalent bonds are one of the predominant forces in most of the fibres. Other intra-polymer forces are the amide or petide groups present in nylon, the benzene ring found in polyethylene terephthalate, ether linkage found in polymer such as polyester, ester group , hydroxyl group and nitrile group [11].

2.4 Inter-polymer Forces

Inter-polymer forces refer to the forces of attraction present between the polymers. These forces of attraction result in the formation of the fibre and play a central role in the strength and mechanical properties of fibres. There are four types of such forces,

1) Van der Waals' forces
2) Hydrogen bonds
3) Salt linkages
4) Cross-Links

2.4.1 Van der Waals' Force

This is the weakest of the inter-polymer forces. Discovered by the Dutch physicist Johannes Diederik Van der Waals'. It can be defined as the weak electrostatic forces of attraction between neutral molecules. These forces are the result of the atoms moving in sympathy with one another in closely adjacent atoms [14]. These forces are weak and do not exist unless the atoms/molecules are in close proximity i.e. closer than

0.2 nm [11]. However, these forces are weak but in the absence of other inter-polymer forces, the Van der Waals' forces play a vital role in determining the mechanical properties of the fibres. Polymers such as polyethylene and polyvinyl chloride only have Van der Waals' forces as inter-polymer forces. Due to the fact that Van der Waals' forces only exist if the polymers are 0.2 nm or closer to each other. Hence, these forces can only exist in the crystalline region of the polymers [15]. This is one of the reasons that polymers which rely only on Van der Waals' forces needs to be very well oriented in order to achieve acceptable mechanical properties. Figure 2.3 shows the two adjacent very closely aligned polyvinylidene chloride polymers, the bracket indicates the occurrence of Van der Waals' force.

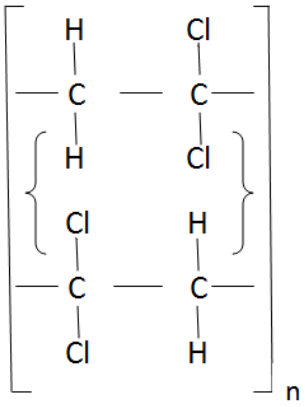

Figure 2.3 Van der Waals' forces indicated by brackets

2.4.2 Hydrogen Bonds

Hydrogen bonds are the weak forces which exist between covalently bonded hydrogen atoms and the strongly electronegative atoms such as oxygen, nitrogen, fluorine and chlorine [16]. In the hydrogen bond, the hydrogen assumes a slightly positive charge and the strongly electronegative atoms e.g. oxygen, nitrogen, fluorine and chlorine assume a very slight negative charge. Figure 2.4 shows an example of hydrogen bond occurring between hydroxyl groups of two closely adjacent cellulose polymers. For hydrogen bonds to exist it is important that the slightly polar atoms are no more than 0.5 nm apart [11].

The predominant number of the hydrogen bonds in a polymer positively influences the mechanical properties such as tenacity, elastic-plastic nature, durability and heat setting properties of the fibre [16, 17].

The presence of the hydrogen bond is also a good indicator of polar sites which attract water molecules therefore resulting in the increased hydrophilicity of the fibre [11].

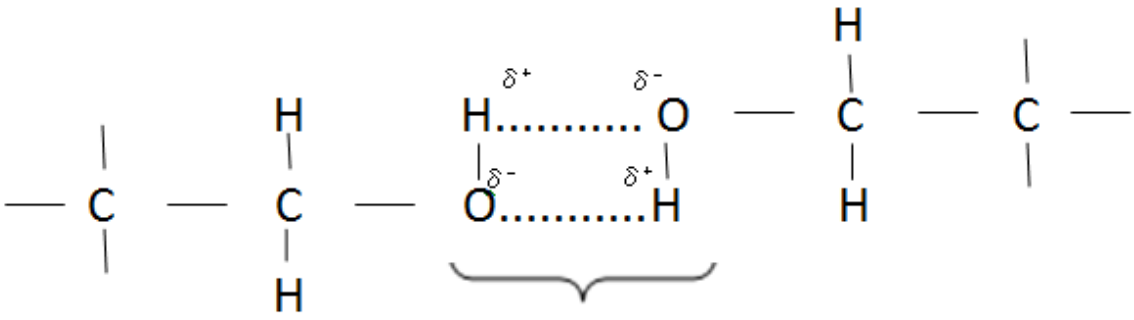

Figure 2.4 Hydrogen bond between two hydroxyl groups on two closely adjacent cellulose polymers

2.4.3 Salt Linkages

The salt links or salt bridges are inter-polymer forces, which exist between the negatively and positively charged radicals in adjacent polymers therefore these linkages are also called electrovalent or ionic bonds [11]. This formation of charged radicals occurs due to complete loss or gain of the electrons. These are strong inter-polymer forces therefore positively contribute to the mechanical properties of fibres [17]. Figure 2.5 shows an example of salt linkage where carboxyl radical having –ve charge formed a salt linkage shown by bracket with a +ve charge amino radical of an adjacent polymer.

These linkages occur at the end terminals of nylon polymers. Protein fibres are another example in which these linkages exit between the polymers.

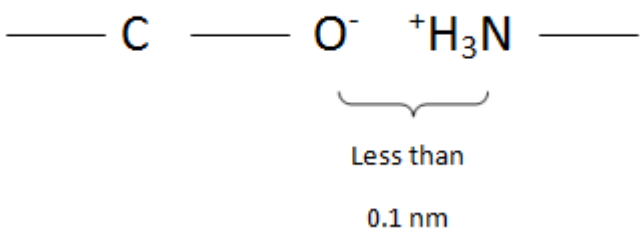

Figure 2.5 Salt linkages formed between the carboxyl radical on one polymer and the positively charged amino group on an adjacent polymer

2.4.4 Cross Links

These are similar to covalent bonds. A covalent bond which exists between the polymer molecules is referred to as a cross link [11]. Wool is an example where cross links are formed between adjacent polymers as indicated by brackets in Figure 2.6. The number of cross-links between the polymers is referred as degree of cross-linking. The degree of cross-linking in a polymer significantly influences the mechanical properties of the fibre. A higher degree of cross linking results in stiffer, more rigid fibre [17]. Synthetic cross linking agents are applied to make easy care textiles [11].

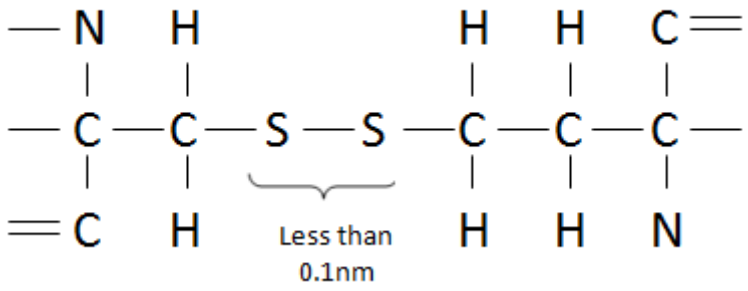

Figure 2.6 Cross links formed between adjacent polymers of wool due to the disulphide bond or cross-link

2.5 Fibre Morphology

2.5.1 Chain Folding

The fibre properties achieved by flexible polymers are less than the theoretical values. Strength is one of the properties that is much lower than the theoretical strength estimated for an ideal uniaxial extended chain structure. An example of such ideal uniaxial fibre structure is shown in Figure 2.7. The ideal fibre structure cannot be achieved due to folding of the long chains during the crystallization[18, 19].

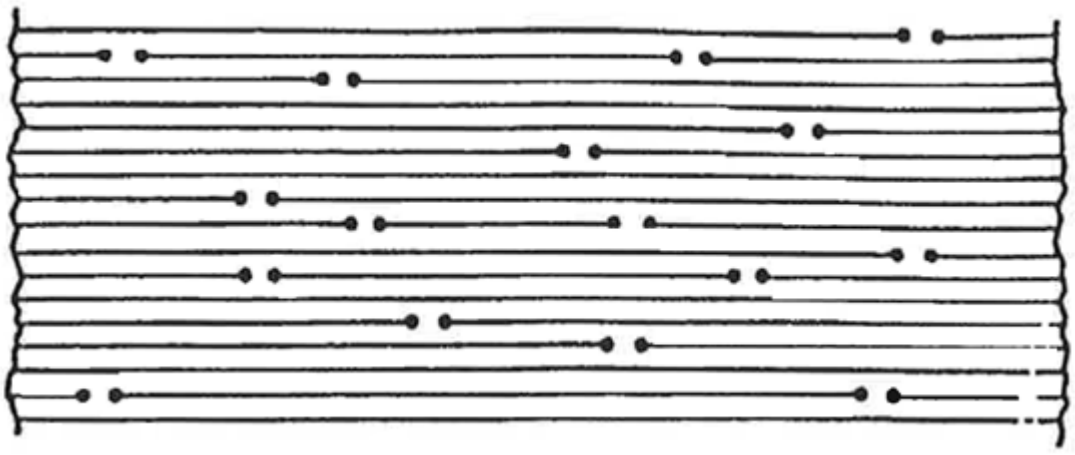

Figure 2.7 Perfect uniaxial fibre structure assumed in the calculations of theoretical strength [4]

These folds can be reduced by drawing but cannot be completely eliminated. Different fibre structures proposed by researchers contain such folds as indicated in Figure 2.8 [20, 21]. Figure 2.8(a) indicates the fibre structure model proposed by Clark and Scott contains such folds. While the model proposed by Fischer and Goddar contains such folds as well in the form of tie molecules. However, reduction of chain folds by drawing significantly improves the properties of the fibres but cannot be employed to achieve ideal orientation and theoretical strength.

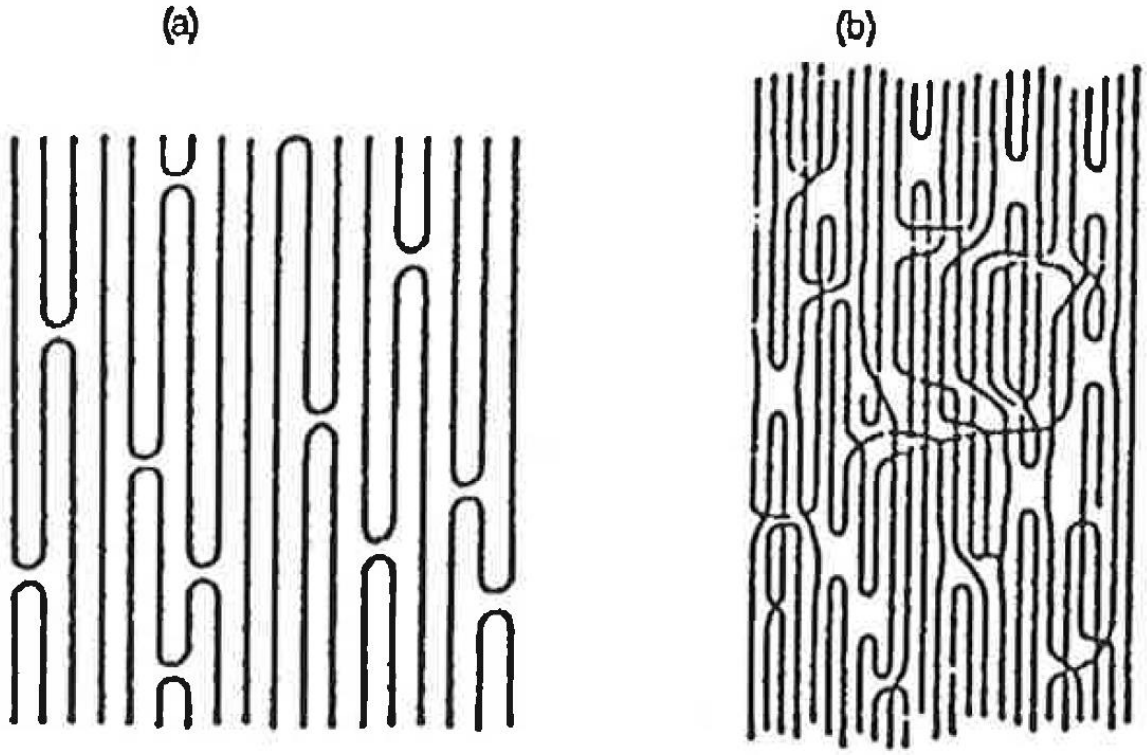

Figure 2.8 (a) fibre structure model proposed by Clark and Scott [20] (b) model proposed by Fischer and Goddar [21]

2.5.2 Microfibrillar Structure

Microfibrils are 6-20 nm thick well defined structural elements. Various studies conducted by using electron microscopy and small angle X-ray scattering (SAXS) led to the same lateral dimensions of microfibrils [4]. The lateral dimensions of the microfibrils decrease with draw ratio. Microfibrils contain polymer molecules with both amorphous and crystalline domains along the fibre axis. Conventional melt spun polymers microfibrils properties are presented in Table 2.1.

Dimension (nm)	PE	PP	Nylon	PET	UHMWPE
Crystallite length		6	6	15-18	60-200
Amorphous length		3	3		5-10
Diameter	16	9-12		16-33	50-100

Table 2.1 Microfibrils properties of conventional and UHMWPE fibres [4]

2.5.3 Inter-Microfibril Interactions

The understanding of inter-microfibril interactions is essential to explain the mechanical properties of polymer fibres. The longitudinal direction of the microfibrils is not well defined in certain fibres such as Nylon and PET. In Nylon and PET microfibrils form an endless interwoven structure. Prevorsek and his co-workers proposed that UHMWPE contains these endless microfibrils [22]. They proposed the PE microfibrils show a unique characteristic of stretching through chain unfolding resulting in stronger microfibrils by forming the intra-fibrillar tie molecules. They further emphasized the importance of this inter- and intra-fibrillar tie molecules in PE though these also exists in Nylon and PET fibres but the importance of these in PE is much more important than the other fibres. They argued that the PE is a special case due to absence of strong inter-molecular forces and very strong primary bonds. The short repeating unit allows the formation of low energy crystal defects, which can easily be activated under applied stress at moderate temperatures. These low energy defects allow the easy lateral displacement of polymer chains. While these conditions do not exist in the case of PET, polyvinyl alcohol (PVA) and nylon in which the lowest energy required to break the weakest molecule is only about 60% of the breaking energy of C-C bonds and the presence of longer repeating units and higher cohesive energies prevent the formation of low energy defects. Hence, the microfibrillar stretching and draw ratio of PE is much higher than any other polymer. The stretching in nylon and PET is the result of microfibril slippage, which results in the formation of tie molecules. However, regardless of these difference in the mechanism of drawing, no melt spun fibre ever

achieved the drawing levels at which the chain folds reduce to the level that exist in surface grown PE [4].

Peterlin [23] proposed the strength of the PE fibre is primarily the result of the strong microfibrils while the inter-fibrillar domain effects are of much lesser importance. However, Prevorsek [22] argues that with nylon and PET fibres the extended chain inter-fibrillar domains are the strongest elements which contribute significantly to the fibre strength and play a vital role in drawn fibre strength. He attributes this to an increased volume fraction of the extended-chain molecules that are formed by the relative displacement of the microfibrils which causes the molecules from the surface of the microfibrils to shear and stretch. Arridge [24] and co-workers proposed that PE fibres behaves as a composite in which the amorphous region is reinforced by the long needle like crystallites.

2.5.4 Chain Rigidity

Chain rigidity has a complex role in the properties of the fibres. It is well established that the chain rigidity affects the fibre's melting point and glass transition temperature. Polymers consisting of higher chain rigidity show higher melting and glass transition temperatures. Rigid chains are a requirement for the liquid crystal. The same molecular criterion is required for the high temperature performance. Despite some differences, these criteria are not contradictory e.g. a fibre design for high strength and high temperature performance requires a nearly straight polymer chain. A small chain cross section will result in a fibre which will also exhibit a liquid crystalline structure in the melt or solution form. Kevlar was originally developed to have a high temperature performance while the experiments of Kwolek [25, 26] demonstrated the exceptional strength of the fibres. They showed that the spinning of aromatic polyamide from anisotropic solution could result in ultra high strength fibres. The development of Kevlar paved the way for the new development in the ultra strong fibres. It has been established that the fibres spun from liquid crystalline solutions exhibit high strength due to the absence or minimum number of chain folding [4].

2.6 UHMWPE Fibres

UHMWPE is one of the strongest fibres currently available [4]. The strength of UHMWPE is 35% more than the aramid fibres on a weight to weight bases. It derives its strength from its very long molecular chains. Although there are no cross linking or other inter polymer forces present other than Van der Waals' forces. The very long molecules give rise to Van der Waals' forces making the fibre very strong. The more complex phenomenon responsible for the exceptional properties of the UHMWPE are explained in detail previously in the fibre morphology section. The comparison of UHMWPE fibres strength with other fibres is represented in Figure 2.9Figure 2.10. The strength of UHMWPE is exceptional comparing to other fibres. The modulus of UHMWPE is twice that of aramid fibres. Due to this exceptional strength UHMWPE is widely used in applications such as bullet proof vests, load carrying ropes, fishing lines, fishing nets, anchor rigs etc.

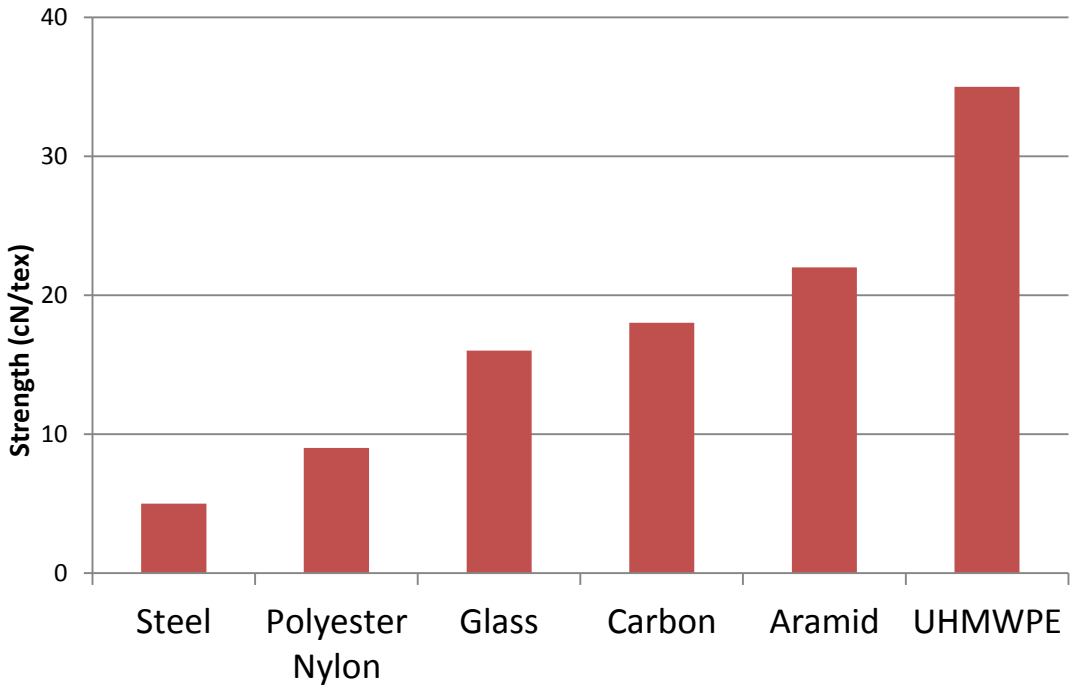

Figure 2.9 Comparison of High Strength fibres [27]

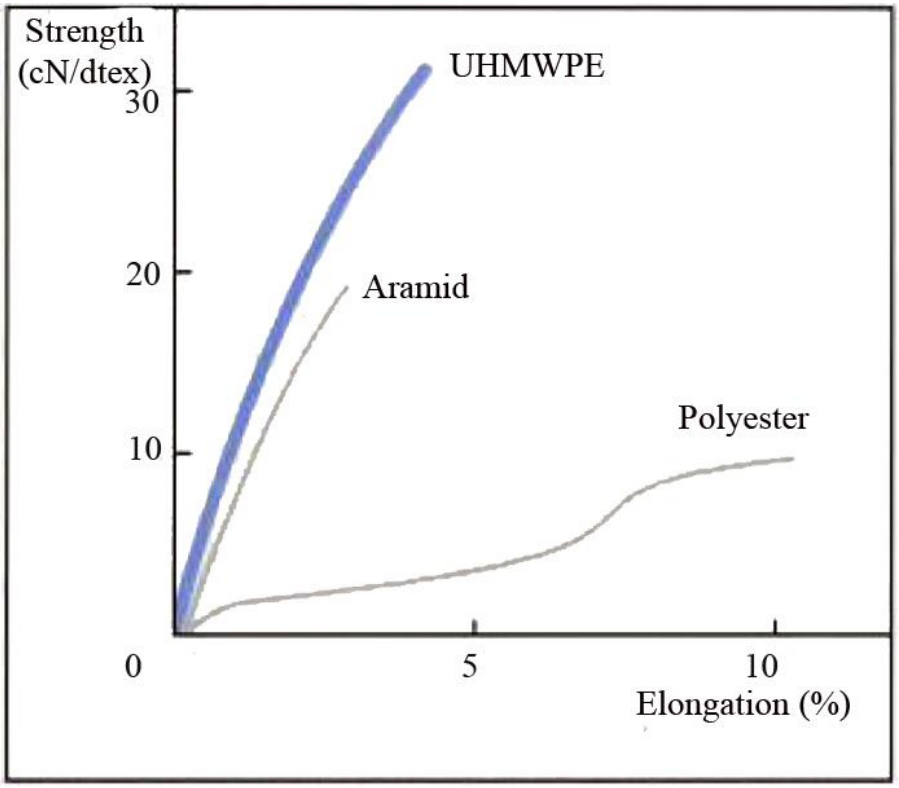

Figure 2.10 Stress Strain chart of UHMWPE compared with aramid and polyester [27]

The density of UHMWPE is lowest amongst the high strength fibres as shown in Figure 2.11. Due to this very low density the fibres float on water which made it a material of choice to be used in fishing and offshore applications. The lower weight combined with floating and cut resistant properties made these fibres perfect material for fishing nets and ropes. Due to their lower weight they are easy to handle and save fuel by reducing the weight to be carried by the fishing boats.

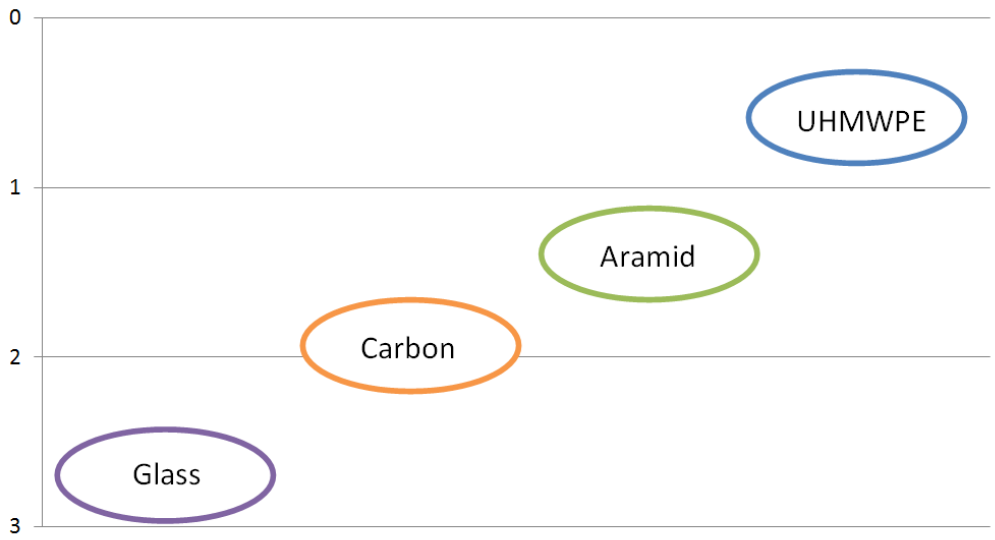

Figure 2.11 Density of high strength fibres [27]

The abrasion resistance and flex life of UHMWPE is better than carbon and aramid fibres as shown in

Figure **2.12**. This high abrasion resistance are widely exploited in the sportswear and leisure wear applications where high abrasion resistance protects the wearer from the injuries. The high abrasion resistance of UHMWPE fibres compared to other high performance fibres meant it performs better than other fibres when used in applications such as load carrying ropes, motor cycle wear, sportswear etc.

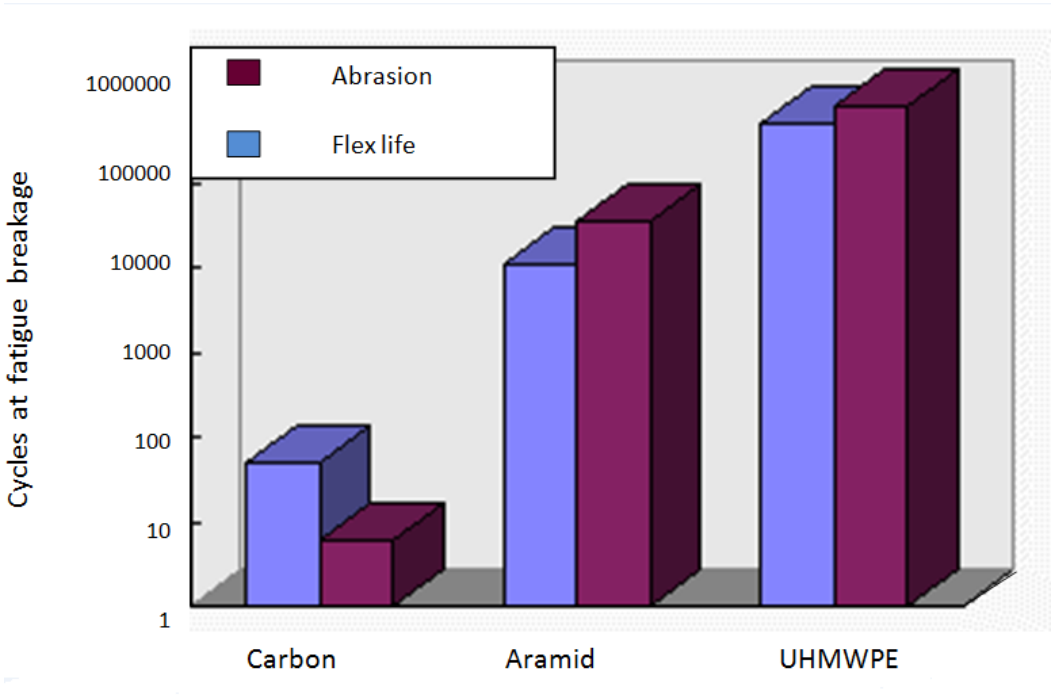

Figure 2.12 Abrasion resistance and flex life of carbon, aramid and UHMWPE [27]

The light stability of UHMWPE is far better than the aramid fibres as shown in Figure 2.13. The aramid fibres losses half of its strength after just 500 hours exposure to the light while at the same exposure time to the light UHMWPE loses less then quarter of its strength. After 1500 hours of exposure to the light aramid fibres loses more than half of its strength while UHMWPE on the same exposure time loses only less than a quarter of its original strength. The superior light stability of UHMWPE meant it can be used in the application involving long term exposure to light. Due to good light stability it is widely used in the offshore applications in the form of sailing cloth and marine ropes.

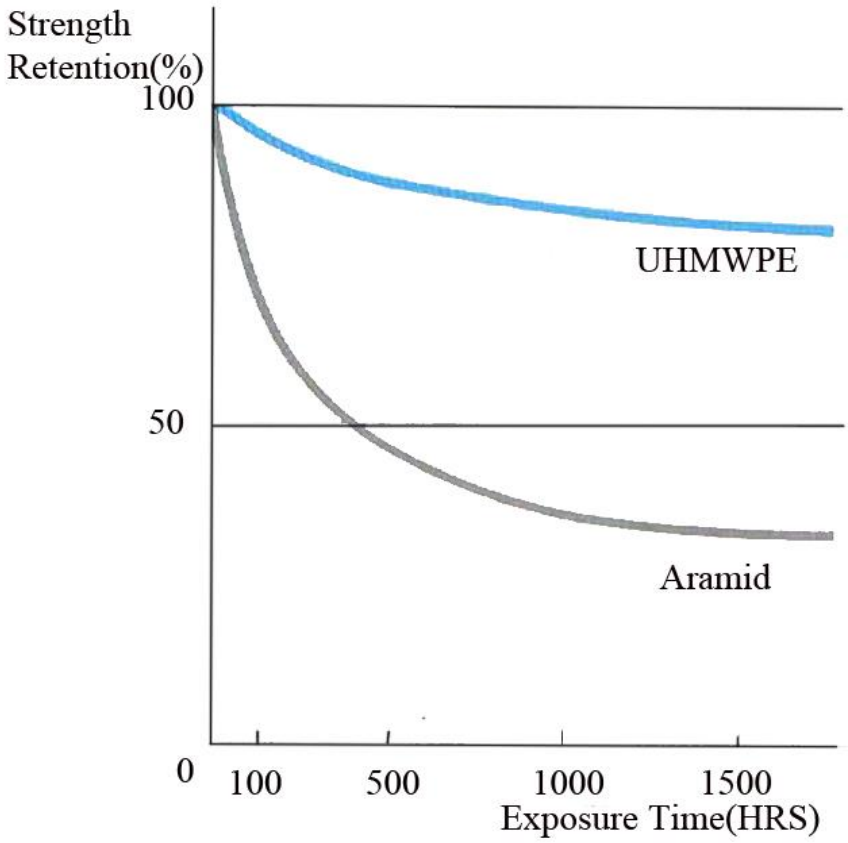

Figure 2.13 light stability of UHMWPE vs. Aramid [27]

The UHMWPE is inert to chemicals with wide range of PH. It retains its strength even on the exposure to very acidic or alkaline chemicals. A comparison of strength retention under wide range of chemical PH of UHMWPE and aramid is shown in Figure 2.14. The very stable chemical structure of the UHMWPE makes it almost inert to the variety of chemicals. The ability of UHMWPE to resist chemical is very useful when used in the form of protective vest for the law enforcement and military where it not only protects the wearer from the ballistic threats but also provides the protection from the host of chemicals. Due to its inert nature it does not degrade when exposed to sea water making it an ideal material for the offshore applications such as anchoring rigs, seismic ropes, fishing nets etc where it is exposed to sea water for very long period.

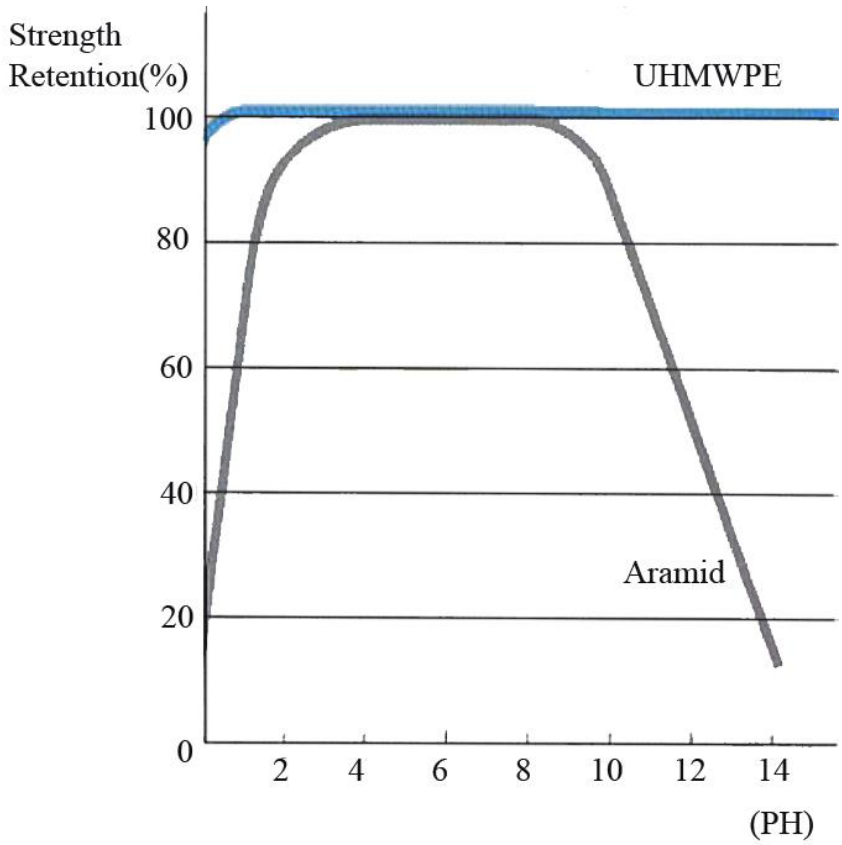

Figure 2.14 Chemical resistance of UHMWPE vs. Aramid at different PH levels [27]

2.7 Methods to Produce UHMWPE Fibres

Although the melt spinning of UHMWPE has been reported [28, 29]. However, in general the extrusion of UHMWPE fibre by conventional methods is very difficult if not impossible. The presence of very high number of polymer chain entanglements per molecule due to very long molecular chains as indicated in Figure 2.15. These chains cannot pass each other during drawing. This high number of chain entanglements also results in the extremely high melt (shear) and elongation viscosities which negatively influence the processability [30]. These chain entanglements also result in a low Melt Flow Index (MFI). Therefore different techniques have been developed to process UHMWPE i.e. hydrostatic extrusion, zone annealing, surface growth method and gel spinning [31]. Gel spinning and the surface growth method are thought to be the most commercially viable processes [4].

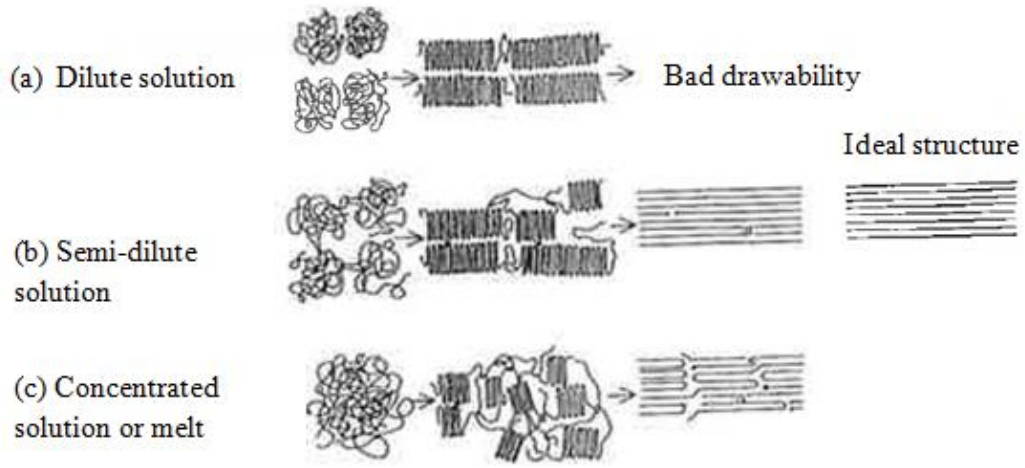

Figure 2.15 Schematic explanation of entanglements [30]

2.7.1 Surface Growth

The surface growth technique of producing UHMWPE fibres is a one step technique in which the fibre is produced in one step unlike other process in which the fibre processing consists of at least two or more stages [10]. The fibre is produced through the coquette flow of a dilute solution by pulling out the growing fibrous crystal [32-36]. There are many designs for such technique; one of the simplest was developed by the Zwijnenburg [33]. The setup shown in Figure 2.16 consists of a beaker and a cylindrical Teflon rotor that is placed in the middle of the beaker. The beaker is connected to a tube through which the seed yarn is introduced in to the system. A tension gauge is installed between the tube and the take up roller to measure tension in the fibre. The fibre is produced by dissolving UHMWPE in p-xylene solution at 130^{o}C. The solution is cooled down and the rotor is set in motion. A seed crystal attached to a fibre is passed through the pipe into the solution. Due to the flow of the solution, the rotating rotor catches the fibre. When it encounters the rotor, it starts to grow; the fibre to which the seed is attached is pulled out. A take-up roller is set in motion and the speed is adjusted equal to the longitudinal growth rate of the fibrous crystal. After the attenuation of the steady state, the process can go on for days [10]. Braham and Keller [32] used the same design to achieve the high modulus. They claimed to achieve the modulus of 262 GPa although there is no mention of the tensile strength in the literature.

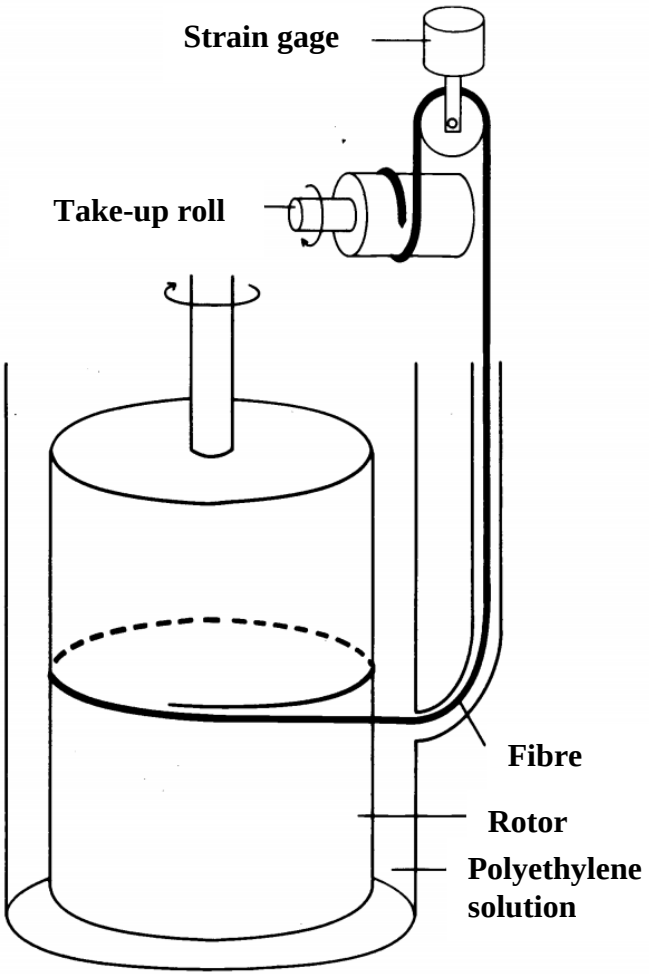

Figure 2.16 Illustration of surface growth setup [10]

A variation of the surface growth method was developed by Kavesh and his co workers [34]. The equipment is schematically present in Figure 2.17. This design provided continuous production of UHMWPE fibres. The solution is prepared in a dissolution vessel and continuously fed to the growth cell. Yarn is produced continuously by pulling it from the growth cell. A pump is attached to the growth cell to recycle the solution and remove the waste. By using this method, they were able to produce fibre with uniform thickness. They claimed to produce the fibre with a tenacity of 30-35 g/d (2.56-2.99 Gpa) and modulus of (81-85 GPa) through this design.

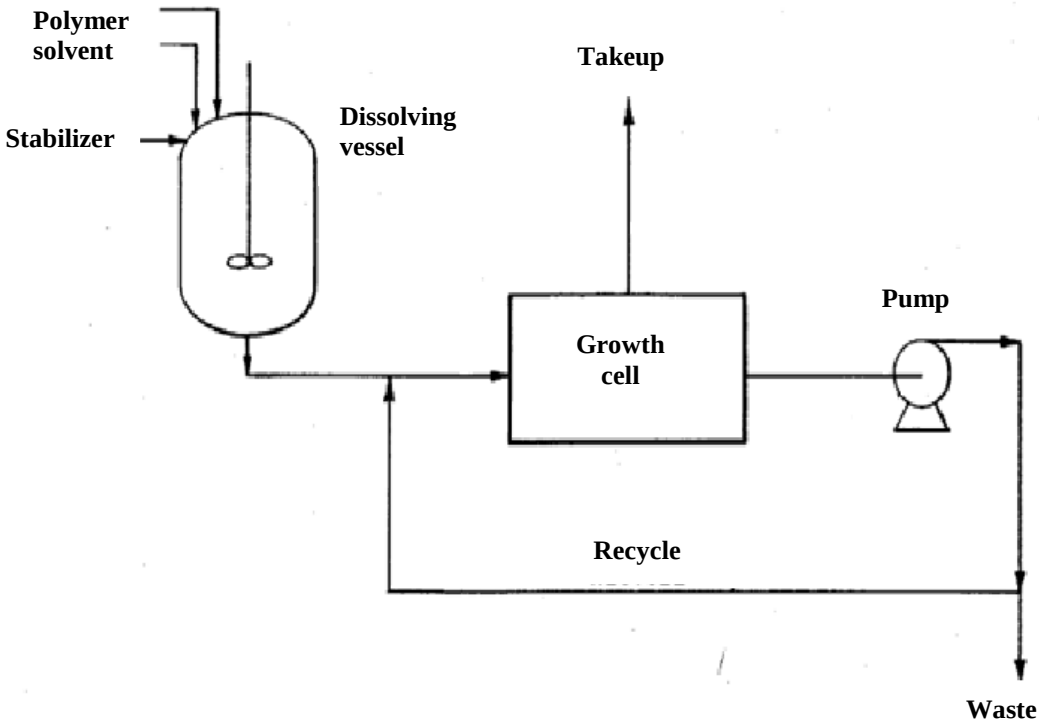

Figure 2.17 Continuous surface growth setup [34]

Prevorsek [4] discussed the advantages of the surface growth method over the other processes. He argued that the experiments conducted by Pennings and colleagues [37] on the surface growth apparatus showed that the exceptionally high modulus and strength can be achieved by flexible polymers such as polyethylene. This demonstrates that the chain foldings were greatly reduced during the surface growth process from the level found in melt spinning. The advantages of this process are as follows

1) Very strong fibres can be produced
2) No solution recovery required as the fibre withdrawn from solution contains very little solvent.
3) Eliminates the use of drawing
4) Due to the elimination of solvent recovery and drawing steps it provides the simplest option for the production of ultra strong fibre.

This process was found to be very useful in producing ultra strong, thick monofilaments for fishing lines, dentals floss and surgical sutures but the process was not suitable for the production of multifilament with fine cross section [4]. The control of the fibre thickness is very difficult in surface growth method.

2.7.2 Gel Spinning

Gel spinning process enables the production of multifilament fibres which was not possible by surface growth method. The thickness of fibres is easier to control in gel spinning. It is a continuous process which makes gel spinning method the most successful method of producing UHMWPE fibres. The theory to produce ultra strong fibre from polyethylene is easy to understand. Normal polyethylene does not contain highly oriented molecules hence fibres could be easily broken. To make it strong the molecular chains needs to be stretched, oriented and crystallised along the axis of the fibre. In addition, the polymer chains must be long enough to have sufficient interactions. Therefore, to achieve ultra high strength fibre, UHMWPE which contains very long polymer chains is used as the starting material. However, due to a very high number of chain entanglements the extrusion of such polymer is impossible. Furthermore, the fibres need to be orientated during drawing but the presence of these chain entanglements significantly reduces the extent to which the fibre can be drawn. To overcome these problems gel spinning is used. The polymer is first dissolved in a solvent where the polymer chains become disentangled and then the solvent is spun through the spinneret. Due to the disentanglement of polymer chains during the extrusion, the extrudate can be drawn to high draw ratios. A high draw ratio results in highly oriented fibres with high tenacity and modulus. Figure 2.18 shows the comparison of orientation of UHMWPE and PE fibre. Due to very long chain length the UHMWPE can be oriented to very high degree unlike normal PE. Gel spun fibres can attain a parallel orientation of more than 95% and a high level crystallinity of up to 85% which gives the fibre superior properties [38].

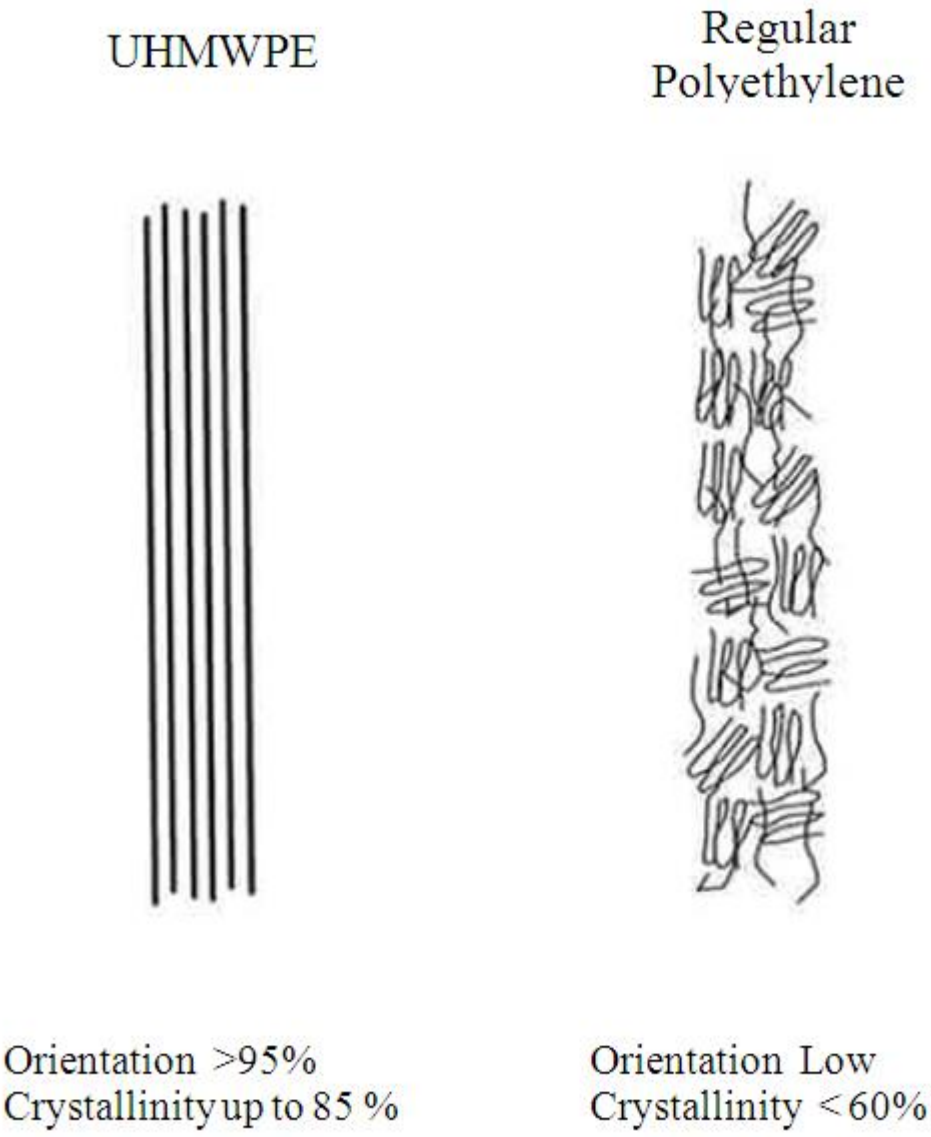

Figure 2.18 Macro molecule orientation of UHMWPE and PE [38]

Different setups were described in the literature to conduct gel spinning described in details in the following sections [30, 38-49]. A schematic representation of a typical gel spinning process is given in Figure 2.19.

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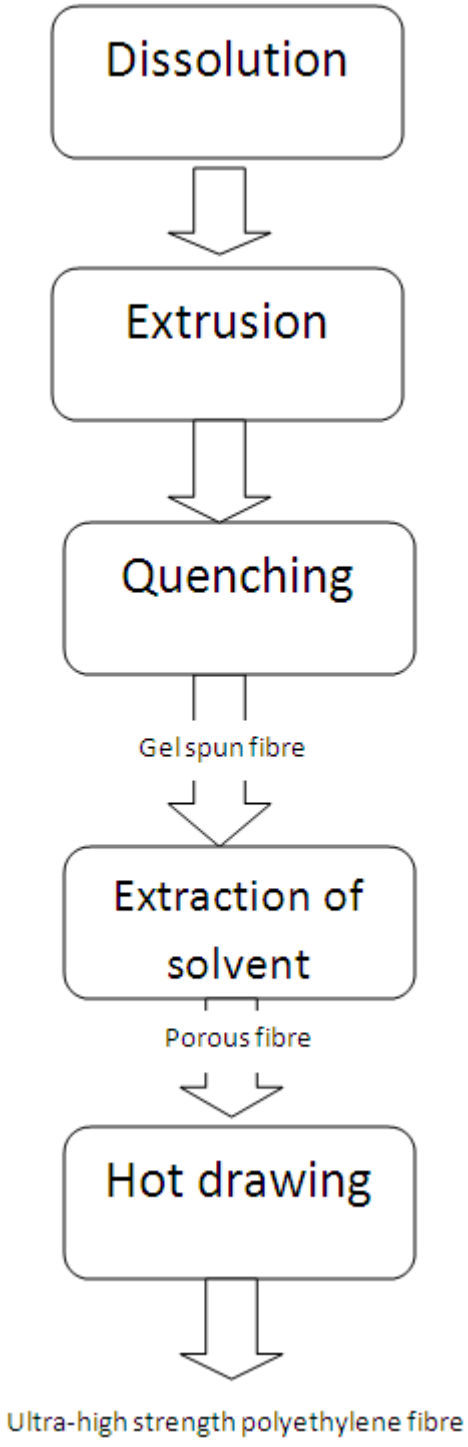

Figure 2.19 Schematic representation of the gel-spinning process

These basic steps could be carried out by employing different techniques, which will be later discussed from the technology perspective. The simplest setup shown in Figure 2.20 may include the following steps

1) A solution of UHMWPE is prepared
2) Solution is fed to the extruder equipped with a metering pump
3) The extrudate is quenched to form gel like fibres
4) The gel fibres are then ultra drawn and the solvent is removed

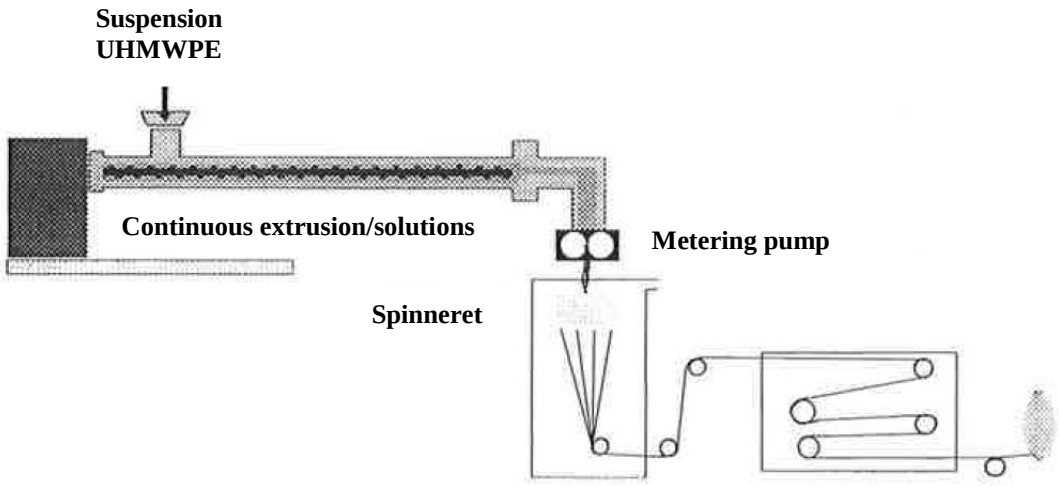

Figure 2.20 Gel spinning process [38]

Different researchers have utilised different solvents and equipment setups each having advantages and disadvantages. The variation includes

- Extrusion techniques
- Solvents
- Solvent extraction/recovery
- Polymer concentration
- Draw ratio

2.7.2.1 Extrusion Techniques

One of the simplest and earliest designs to produce UHMWPE fibre by gel spinning was designed by Smith and Lemstra [39, 50-52] in which they used equipment similar to a ram extruder. Figure 2.21 shows the systematic setup. The solvent was maintained at 130^{o}C and then pumped through capillaries with diameter ranging from

0.5 to 1.0 mm and a length of 3.0 mm. The extrudate was passed through cold water to form gel fibre. Their setup consists of a hot-air oven at 120^{o}C. The gel filament leaving the cold water was subsequently drawn yielding highly oriented polyethylene fibres.

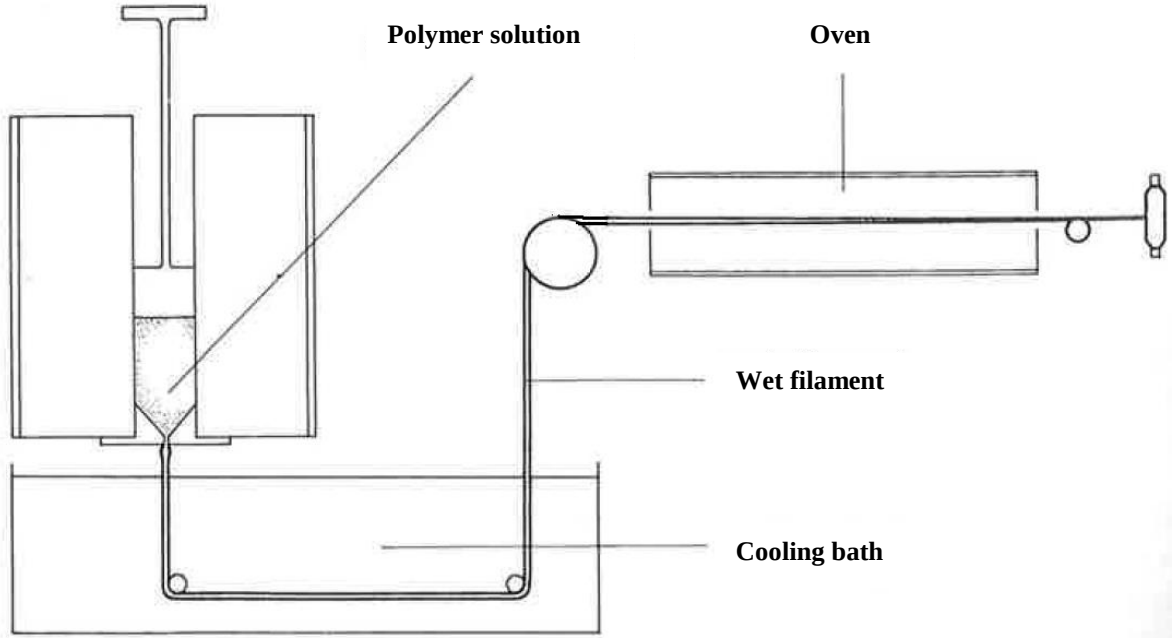

Figure 2.21 Smith and Lemstra setup for UHMWPE extrusion [39]

In their US Patent Da Cunha et al. [53] described gel spinning of UHMWPE fibre by utilising a single screw extruder. Figure 2.22 demonstrates a schematic of their design. The suspension of UHMWPE in solvent is fed to the extruder by means of a pump. The extruder they described was a single screw extruder with L/D 30 to 35. Their design consist at least three heating zones set at 240^{o}C, 250^{o}C and 260^{o}C respectively. The heating converts the suspension into gel, which is then fed to the spinneret through the gear pump to control the gel flow rate. The extrudate is then passed through the water, which is kept at -5 to +5^{o}C. The filaments are then taken up on the spools for further processing.

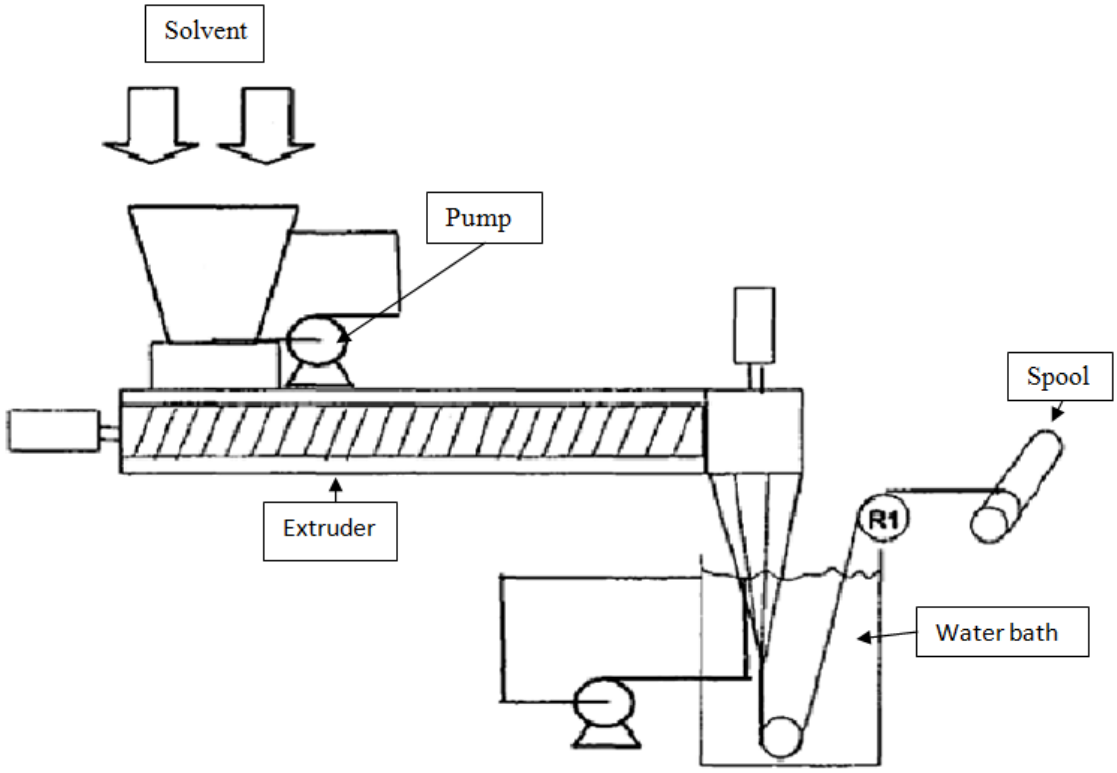

Figure 2.22 Gel spinning design described by Da Cunha et al. [53]

Gel spinning was performed by Yamin Wang et al. by dissolving the UHMWPE in paraffin oil at 170^{o}C. The solution was then pumped through the spinneret into the cold water to form the gel fibres. The mechanism of pumping the solution is not further explained in the paper [54].

A different approach was adopted by Smook et al. than the previous researchers for gel spinning of UHMWPE. Figure 2.23 shows schematic of the setup. Their process consisted of intermediate steps, which provide flexibility by providing no fixed time between two subsequent steps. In the first step, the solution of UHMWPE was prepared in paraffin oil by dissolving polymer at 150^{o}C for 48 hours. The solution was left to cool down to ambient temperature that converts the solution into a wax-like substance. In the second step, the wax-like gel was chopped into small pieces. In the final step, the pieces of UHMPWE gel were fed into the screw extruder at 170^{o}C fitted with different dies [55].

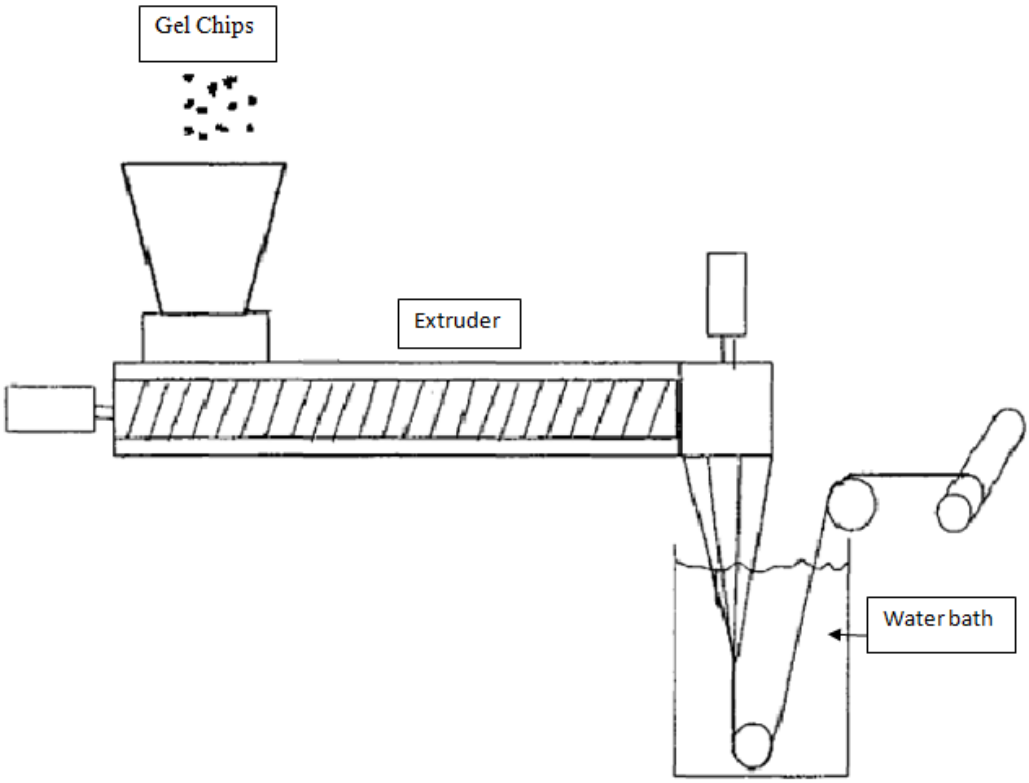

Figure 2.23 Schematic explanation of Smook et al. gel spinning setup [55]

In their patents Kavesh et al. described a gel spinning process [43, 45]. They used a glass vessel equipped with a PTFE stirrer. The UHMWPE polymer and the paraffin oil were loaded into the vessel with antioxidant. The vessel was sealed under nitrogen pressure and heated to 150^{o}C with stirring. The solution was stirred for 48 hours at 150^{o}C then cooled to room temperature. Phase separation occurred in the solution at room temperature resulting in two phases; one phase of very low concentration and a second rubbery gel with higher concentration. The rubber gel was collected, cut into pieces and fed to a screw extruder with 21/1 L/D ratio. The extruder was equipped with a single hole conical die. In this experiment, the compression of the extruder caused the exudation of the paraffin from the gel, which was discharged from the hopper.

In the same patent another process was described. They employed an oil jacketed, double helical mixer. They charged the mixer with UHMWPE and oil. The mixer was heated with agitation at 20 rpm to 200^{o}C. The mixer was kept under nitrogen pressure for two hours. The solution was maintained for 2 hr after reaching 200^{o}C. A single hole, capillary spinning die of 9.5 mm length and 2 mm diameter was fitted at the bottom discharge of the helical mixer. The extrusion was performed by applying

nitrogen pressure together with the rotation of the helical mixer blades. The solution extruded from the die passed through a 33 cm air gap and then quenched into the water bath. Following quenching the extrudate formed gel fibre which was collected over the bobbin for further processing [43, 45, 49].

A slight variation of the Kavesh et al. method [43] was described by Harpell et al. to produce gel spun fibres in their patents [46, 56]. The small variation in the process from Kavesh et al. process was the introduction of a multifilament die in contrast to the previous processes. The die consisted of 16 holes each with 0.75 mm diameter and 22.5 mm length. The other variation they described in the patent was the percentage of polymer. Their process made the production of multifilament polymer possible.

Kavesh in his patent utilised a fifteen gallon drum installed with a three inch diameter propeller agitator. According to the invention, the drum is charged with mineral oil, UHMWPE and antioxidant. The agitator is rotated with 1725 rpm to get the uniform dispersion. The drum is connected to a positive displacement piston pump at the bottom opening. The other end of the pump is connected to a screw extruder. The screw extruder is maintained at 290^{o}C along the whole length of the screw. The extruder is fitted with a gear pump to control flow rate to the die head. This patent also discussed a setup which replaced the piston pump with a centrifugal pump. Extrusion was conducted by using a centrifugal pump which resulted in a highly variable concentration and dissolution in the extrudate. The homogeneity of the solution could not be achieved even when the screw speed was altered from 20 to 400 rpm and the temperature of the extruder from 200 to 290 ^{o}C. It was suggested in the patent that this could be due to the lack of feed pressure in the extruder as the UHMWPE solution has lower viscosity in solution form than in the gel [40].

A comprehensive gel spinning design was described by Izod et al. containing a dissolution vessel, extruder, drawing, solvent extraction and solvent recovery as shown in Figure 2.24. The patent described a design consisting of a vessel installed with a stirrer which was fed with UHMWPE and mineral oil via a feed line. The solution of UHMWPE polymer and mineral oil was stirred until it formed the slurry which was then transferred to a vessel equipped with helical agitator blades. The heat was provided with the agitation to convert the slurry into solution. From the intensive mixing vessel, the solution was transferred to the extruder, which was fitted with a gear

pump to control the solution flow. The gear pump fed the solution to the dies at a controlled rate. The extrudate from the spinneret was then passed through the air gap followed by the quenching bath. The quenching of the extrudate converted it into a gel-like fibre. The fibre was then conveyed to another chamber called the solvent extraction chamber. At this stage, paraffin was removed from the fibre by using a solvent which was solvent for paraffin but not for polyethylene. The fibre was then taken to the next chamber which contained a volatile washing liquid to remove the extraction solvent from the fibre. The fibre then entered the drying chamber where the washing liquid evaporated to give dried fibres. The whole system was equipped with solvent recovery systems, which recycled the solvent back to the system [47].

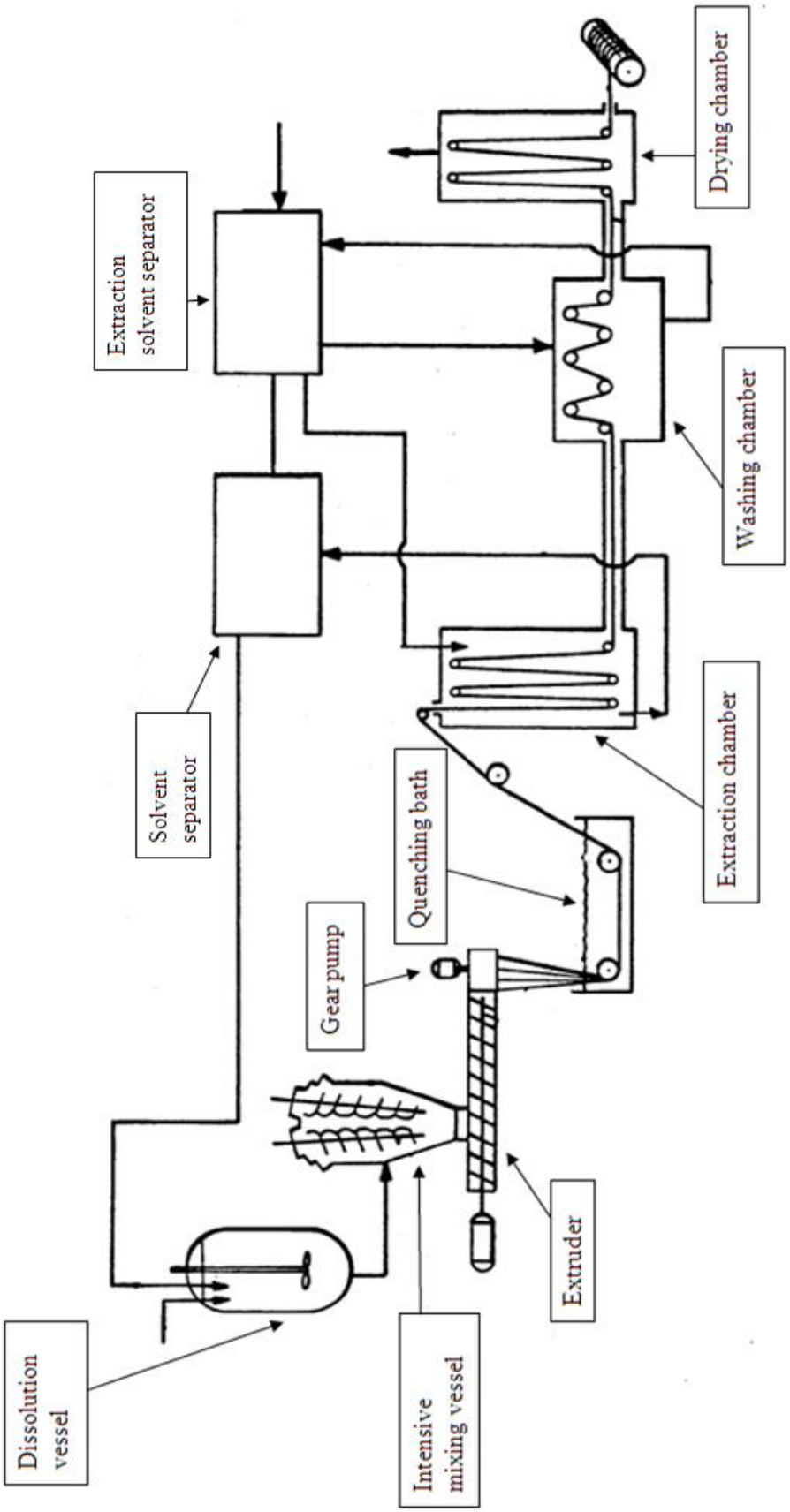

Figure 2.24 Schematic description of the Izod et al. gel spinning setup [47].

The design by Simmelink et al. for the gel spinning of UHMWPE, unlike the previously discussed design consists of a twin screw extruder and more volatile chemicals [48]. In the examples given in this patent, the gel spinning was carried out by utilizing decalin as a solvent for the preparation of solution. The solution was extruded through a twin-screw extruder fitted with gear pump to control the flow. The spinneret used for the fibre extrusion contained 64 holes, each having a gradual decrease in the diameter from 3 to 1 mm over a length of 0.17 cm followed by a section of uniform diameter with a L/D of 10. The extruded fibres from the spinneret passed through an air gap where a certain amount of stretching took place followed by quenching in water bath. Fibres were then taken to an oven where drawing and drying of the fibre was conducted.

A gel spinning process described by Hu et al. consists an untwisting pan. Untwisting pan as explained in the invention can be any of the following: high-speed dispersion machine, agitator (intensive mixing vessel), colloid mill, homogenizer, venturi or any of the combinations. According to their invention the white oil and UHMWPE is fed into the untwisting pan at room temperature. The pan is operated for 10 min at the speed of 2000 S^{-1} under nitrogen protection to form a homogenous emulsion. The solution is fed to a double screw extruder. The solution is filtered and spun into the gel filament through a spinneret followed by stretching and drying [57].

Design described by Tam et al. consists of an agitator mixing tank in which mineral oil and UHMWPE is fed to prepare a slurry at 35-38^{o}C. The slurry is continuously fed into the feed hopper of an intermeshing co-rotating twin screw extruder. The feed hopper is kept flooded under the nitrogen blanket. In the example that explained in the patent, the screw has the diameter of 40 mm. The screw elements having the root diameter of 32.52 mm were all forwarding conveying elements. The screws were operated at 250 rpm. The extruder was heated to 260^{o}C. The resident time of the liquid was 1.15 min. The extruder is fitted with a gear pump to control the flow of the solution. The solution passing through the gear pump passed through a vessel consisting of a long network of 46.7 feet (14.17 meters) pipes with an internal volume of 29.212 cm^3. The resident time of solution in the piping network was 24 min. The UHMWPE solution leaving the vessel is passed through a gear pump followed by a spin block and spinneret having 181 holes of 0.036 inch (0.914 mm) diameter. The solution is stretched to 1.8:1 in the air gap before entering the water bath at 9.5^{o}C. After

quenching, the solution turns into the form of gel fibres. The gel then goes through several drawings and the solvent extraction process [58, 59].

Magno's gel spinning process is unique due to its utilization of a helical mixer on its own for extrusion. In the previously described gel spinning process, the helical mixer was just used as a mixing aid. According to this design the stainless steel jacketed vessel equipped with a paddle stirrer as shown in Figure 2.25 is charged with UHMWPE, mineral oil, aluminium stearate and antioxidant. The temperature of the vessel is increased 1^{o}C/min to 150^{o}C. The solution is stirred by a rotating paddle stirrer at 10 rpm under nitrogen pressure of 2 psi for 15 hours. This treatment resulted in a slurry mixture. The slurry is then cooled to 70^{o}C. The helical mixture is preheated to 70^{o}C and slurry from the mixing vessel is transferred to the preheated helical mixture. The helical mixture is rotated to 5 rpm with a nitrogen blanket of 2 psi pressure. The temperature of the solution is then increased by 2^{o}C/min to 155^{o}C. After reaching 155^{o}C the solution is kept at this temperature for 30 min with rotation of 10 rpm. The temperature of the solution is again increased to 180^{o}C at the rate of 2^{o}C/min and maintained at this temperature for 30 min. To extrude the fibre, the rotation speed is increased to 15 rpm and the nitrogen pressure is increased to 12 psi. The bottom opening of the helical mixture is fitted with a spinneret which is heated to 168^{o}C and maintained at this temperature during extrusion. Due to the rotation, gravitation and nitrogen pressure the slurry passes through the metering pump and extruded through the spinneret. The extrudate is then passed through the water to from gel fibre which is further processed to form finished fibres [60].

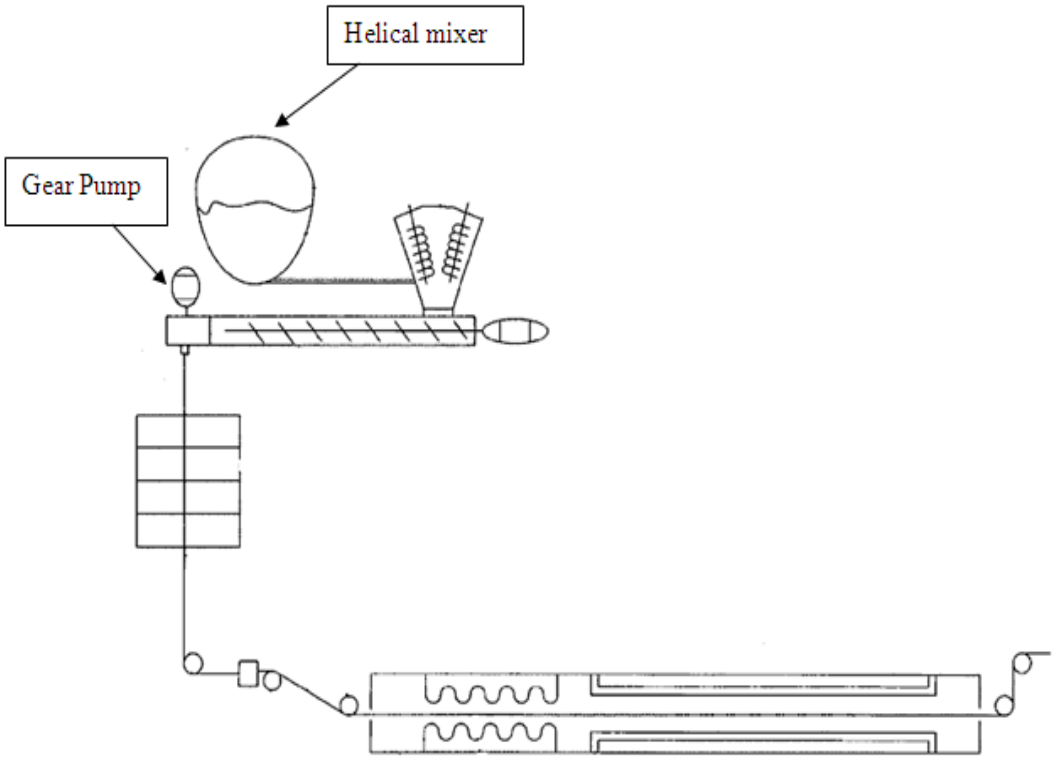

Figure 2.25 Magno's gel spinning setup [60].

A relatively simple form of the previously discussed Magno's process [60] was described by Chen et al. The schematic of their design is shown in Figure 2.26. In their design the solution is prepared by heating polymer and solvent to 140^{o}C with agitation. The agitation is maintained at 140^{o}C until complete dissolution of the polymer is achieved. The solution is then fed to the spinneret via a metering pump. The extrusion is carried out at 1 KPa pressure through a single capillary hole of 1.5 mm diameter which is maintained at 150^{o}C. The extrudate is passed through an air gap of 5 cm and then through the water bath which converts the solution into the gel fibre. The gel fibre is then extracted and drawn to achieve finished fibre [41].

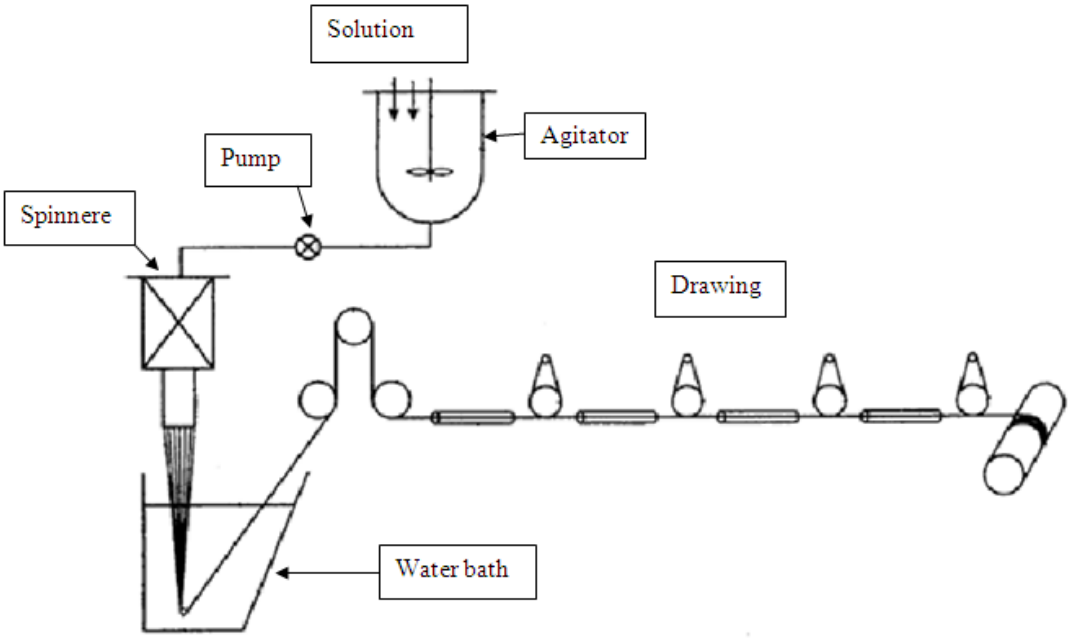

Figure 2.26 Chen et al. gel spinning setup [41]

2.7.2.2 Solvents

It was discussed previously that UHMWPE has a very low melt flow index (MFI) which makes the extrusion of UHMWPE by conventional methods very difficult. To overcome this limit, gel spinning is carried out where the solution of UHMWPE polymer is made in an appropriate solvent. Solvent plays vital role in gel spinning though it is just required as a medium to assist the extrusion of fibre while it also helps to disentangle the polymer chains resulting in increasing the draw ratio hence improving the strength as suggested by Smith and Lemstra [61]. Many researchers have experimented with different types of solvent that includes Paraffin oil, decalin, dodecane, kerosene, p-xylene and trichlorobenzene. Researchers have used different solvents to prepare the solution by employing different equipment.

Smith and Lemstra in their patent explain a gel spinning process in which they used decalin as a solvent for the UHMWPE. They prepared the solution by dissolving 2%w/w of polymer in decalin at 150^{o}C [39, 50-52]. The solution was then extruded by pumping the solution at 130^{o}C through the spinneret. The extrudate was then passed through the water bath to produce gel fibres.

Decalin was utilised by Matsuo et al. to prepare blend films of UHMWPE and UHMWPP by gelation/crystallization from the solution. They prepared the blends by

mixing different chosen concentrations of polymers in decalin. The mixture was then heated to 150^{o}C for 40 min under nitrogen with a small quantity of antioxidant to avoid oxidation. The films were prepared by pouring the hot homogenised solution over an aluminium tray surrounded by ice water. The quenching converted the solution into a gel [62, 63].

Manley and Masuo described a slightly different process for producing a solution of UHMWPE from decalin. They prepared the solution by heating the mixture of polymer and decalin at 165^{o}C for 5 min followed by heating at 158^{o}C for 55 min. This resulted in a homogenised solution which was poured over an aluminium tray surrounded by ice water to form the gel [64].

Design described by Marissen et al. uses a twin-screw extruder to prepare the solution in contrast to previous processes in which the solution was prepared separately in a vessel. According to their process, the UHMWPE is mixed in decalin in a concentration of 9 % by weight. The mixture was then fed to a twin screw extruder where it was heated to a temperature of 180^{o}C, hence the solution was prepared inside the extruder which is fitted with a gear pump and spinneret to extrude the fibres [65].

Solution of UHMWPE prepared by Anton et al. by mixing the polymer with decalin at 80^{o}C and heating it further to 140^{o}C with mechanical stirring. On the emergence of gelation at 105^{o}C stirring was stopped and the solution was left to heat at 140^{o}C for 30 min. The solution was then air cooled to room temperature to form gel [66].

Kalb and Pennings in one of their experiments utilised dodecane as a solvent for UHMWPE. They prepared the polymer solution by dissolving polymer and an antioxidant in dodecane under constant slow stirring at 150^{o}C for 48 hours [67].

It has been reported by Zhang et al. that kerosene can be utilised as a solvent for gel spinning of UHMWPE by preparing the polymer solution of UHMWPE in kerosene. However, there is no mention of the temperature and duration. The extrusion was carried out by a self made mini extrusion machine while there were no details provided of the machine [9].

p-xylene was utilised by Kunugi et al. as a solvent for UHMWPE. They prepared the solution by dissolving polymer in p-xylene at boiling temperature [68-70].

Pennings and his co-workers used paraffin oil for most of their experiments although they also used dodecane, decalin, tricholobenzene and p-xylene [10]. They carried out the solution preparation by mixing polymer into paraffin solution. The mixture was then heated to 150^{o}C for 48 hours with mild stirring [55, 71-73].

Paraffin oil as a solvent for the preparation of the UHMWPE solution was also utilised by Wang et al. Their process consists of dissolving UHMWPE at 175^{o}C in paraffin oil with slow stirring. To avoid oxidation, antioxidants were used and the solution was flushed with nitrogen [54].

A process described by Izod et al. for the preparation of an UHMWPE solution utilising paraffin oil. However, this process is complicated and used several machines. In their process paraffin oil and polymer were fed to the vessel equipped with an agitator. The agitation converts paraffin oil and polymer into a slurry, which is then transferred to an intensive mixing vessel equipped with a helical mixer. The temperature of the intensive–mixing vessel was raised to 200^{o}C to complete the dissolution of the polymer forming polymer solution which was then fed to extrusion equipment [47].

In the patent Tam et al. described a different process for the preparation of the polymer solution. In this process the paraffin oil and UHMWPE is fed to an agitator which forms the slurry that is then fed continuously to an intermeshing double screw extruder. Unlike the previously described process, the dissolution takes place in the extrusion machine. The extruder is heated to 260^{o}C. The residence time of the solution inside the extruder is kept at 1.15 min [58, 59, 74].

Process described by Hu et al. for preparing the UHMWPE solution employs paraffin as solvent. The solvent and polymer are fed to an untwisting pan (intensive mixing vessel). The oil and polymer are mixed in the intensive mixing vessel for ten minutes then it is transferred to an unidirectional double screw extruder which is heated at 250^{o}C where the dissolution of polymer takes place resulting in a homogenous solution [57].

A simple process to prepare the polymer solution from paraffin oil was explained by Da cunha et al. In their process a suspension of UHMWPE and paraffin was sent to a single screw extruder by means of a pump. The extruder having three

heating zones was heated at 240^{o}C, 250^{o}C and 260^{o}C. The polymer completely dissolved inside the extruder forming a homogenous gel [53].

Magno also used paraffin oil for the preparation of a polymer solution of UHMWPE. The process starts with the mixing of polymer and paraffin oil in a mixing vessel equipped with a paddle stirrer. The mixture is heated to 150^{o}C with constant stirring for hours. This resulted in slurry which is then transferred to an helical mixer where the helical mixer is rotated and an appropriate temperature is applied to get the homogenous solution [60].

Kavesh and his co-workers used paraffin for gel spinning of UHMWPE. There are many patents by Kavesh and his co-workers in which different equipment was used for the gel spinning where all the experiments were carried out utilising paraffin oil [34, 40, 43, 45, 46, 49, 56].

2.7.2.3 Solvent Extraction/ Recovery

Extraction of the solvent is an important process. After the gel spinning, fibre contains a significant amount of solvent, which needs to be removed. Depending on the solvent used in gel spinning different extraction solvents are used. The solvent to be used as an extraction solvent should be able to dissolve the spinning solvent but should not be a solvent for polyethylene. The extraction solvent should have a low boiling point so that after the extraction of the spinning solvent a simple drying process could remove the extraction solvent. Due to the diverse use of spinning solvents, there is a wide variety of extraction solvents investigated by many researchers. Some of the spinning solvents with high volatility do not require extraction solvents; they can be removed by mechanical removal followed by drying.

Pennings and his co-workers chose n-hexane as the extraction solvent for the removal of paraffin oil from gel fibre. They extracted the paraffin oil by immersing the fibres in n-hexane which replaces the paraffin oil with n-hexane. Fibres are then vacuum dried to remove n-hexane [55, 71].

Hexane was employed by Da Cunha et al. as an extraction solvent for paraffin oil. The fibres are wound over spools or reels and the solvent is forced to flow through the spools or reels as shown in Figure 2.27. The extractor is sealed and is operated at a

maximum temperature of 70^{o}C. The extraction is conducted in multiple stages followed by drying [53].

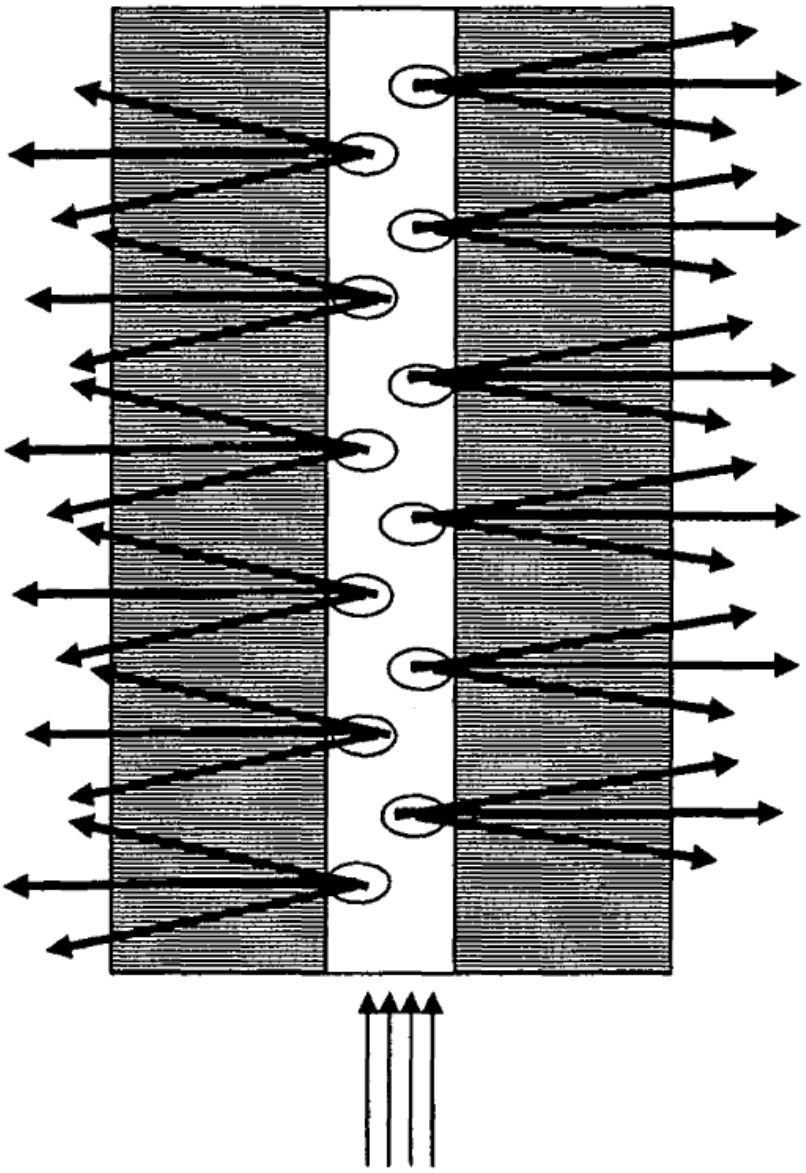

Figure 2.27 Flow of solvent during solvent extraction of the process [53]

Hexane was also utilised by Kavesh et al. as an extraction solvent for paraffin oil. The process explained in their patent consists of two stages. In the first stage the paraffin oil is extracted from the fibre and replaced by hexane followed by the second stage in which hexane is vacuum dried at 50^{o}C [43, 49].

They also used trichloro-trifloroethane (TCTFE) as an extraction solvent. The fibres are wound on the bobbins which are immersed in TCTFE solvent. Immersion of gel fibre containing paraffin oil into TCTFE exchanges the oil present in the gel with

TCTFE as a liquid constituent of the gel. The TCTFE is then evaporated by unwinding the gel fibre at 22^{o}C to 50^{o}C [43, 49].

If the solvent used for the preparation of the gel has a low boiling point it is possible to remove it without utilizing any extraction solvent. Sawatari and Matsuo utilised decalin to prepare the polymer solution. Due to the lower boiling point of decalin they were able to remove it by allowing it to evaporate at ambient temperature followed by vacuum drying for 24 hours [62, 63].

Matsuo and Manley published a technique which varied slightly from the previously described method although their gel was also prepared utilising decalin as the solvent for the polymer. They allowed the decalin to evaporate for 14 days. The gel was then immersed in ethanol for 1 day to remove any remaining traces of decalin followed by 6 days drying [64].

The Lemstra and Smith design combined drawing and solvent removal in one-step by utilising a hot oven. The solvent utilised in this design was decalin. Due to high volatility of decalin they were able to extract it by passing gel fibre through the hot oven at 120^{o}C where drawing also takes place [39, 42, 50].

The same method used by Lemstra and Smith was utilised by Simmelink et al. to extract the solvent. Gel fibres were taken-up into an oven maintained at 90^{o}C. As fibres are stretched in the oven the evaporation of the solvent also takes place [48].

Cyclohexanone was employed by Chen et al. to remove spinning solvent from the gel fibres. The gel fibres were passed through an extraction vessel containing cyclohexanone where spinning solvent is replaced by cyclohexanone. The following drawing process at high temperature evaporates cyclohexanone leaving dried fibres [41].

Cyclohexane was used by Tam et al. to extract paraffin oil from gel fibres. Gel fibres were passed counter-current to a stream of cyclohexane at ambient temperature. Fibres are subsequently passed through a dryer to evaporate the cyclohexane [58, 74].

Magno's process for the extraction of spinning solvent employs xylene. To extract spinning solvent gel fibres are wound on the spools, which are immersed in xylene for 24 hours. Fibres are then re-spooled and again immersed in xylene for 24 hours. The same process is repeated for a third time without applying tension. Spools

are then unwound and rewound while passing the fibres through a hot air flow to dry the fibres. This spooling and re-spooling is repeated five times with hot air drying until fibres are completely dried [60].

Gasoline was used as an extraction solvent by Zhang et al. in their experiments. They prepared the gel fibre by utilising kerosene oil with a boiling point approximately 160-180^{o}C. The kerosene is first removed while passing through a quenching bath containing water. Due to the phase separation that occurs in the gel filament when the temperature is reduced, the solvent starts to separate from the gel below the gelation point. After some time the gel is left with a certain amount of kerosene which is then extracted by gasoline which itself is removed by allowing it to evaporate at room temperature [9].

De Boer and Pennings used boiling chloroform to remove spinning solvent from extruded fibres followed by drying at 50^{o}C under vacuum for 24 hours [75].

The removal of solvent was carried out by Zhu et al. by immersing gel in the methanol for 24 hours followed by vacuum drying to remove traces of solvent and methanol [52].

The most comprehensive solvent extraction process was described by Izod et al. in their patent [47]. In their design, gel fibres are taken into a solvent extraction chamber which contains extraction solvent, which is a solvent for paraffin and water at certain temperatures it could be diethylene glycol monobutyl ether at 0 to about 25 ^{o}C. Paraffin is replaced by extraction solvent in the solvent extraction chamber. The extraction solvent in the extraction chamber containing paraffin oil is conveyed to a solvent separation chamber where spinning solvent and extrusion solvent are separated. Spinning solvent is conveyed to the solution agitator vessel where spinning solution is prepared. Extraction solvent is conveyed back to the solvent extraction chamber. Fibres leaving the extraction chamber consist of a very small amount of paraffin oil and significant amount of extraction solvent. Fibres are conveyed to a washing chamber to wash off the extraction solvent; washing is performed by using water or alcohols. The washing solvent must be more volatile than the extraction solvent. Fibres are washed in the washing chamber where the extraction solvent is removed. The washing solvent containing extraction solvent is conveyed to the solvent separation chamber where washing solvent and extraction solvents are separated. Extraction solvent is taken to the

solvent extraction chamber while the washing solvent is taken back to the washing chamber. Fibres leaving the washing chamber contain washing solvent which is removed by drying [47].

Prevorsek studied the effect of different extraction solvents on the fibres. He experimented with nine solvents: diethyl ether, n-pentane, methylene chloride, trichloro trifluoroethane (TCTFE), n-hexane, dioxane and toluene, having varying boiling points from 34.5^{o}C (diethyl ether) to 110^{o}C (toluene). He reported interesting phenomenon. The fibres extracted with low boiling point extracting solvents were cylindrical then the fibres extracted with solvents with higher boiling points. The shape and surface texture of the extracted fibres degrades from a smooth cylindrical form proportion to the extracting solvent boiling point. Hence, fibres extracted with diethyl ether presented nearly cylindrical shape. However fibres extracted with toluene resulted in C-shape cross section after drying [4].

2.7.2.4 Polymer Concentration

Polymer concentration is one of the most important factors for an economic process. As discussed previously, the extrusion of UHMWPE is difficult by conventional methods due to its very high melt viscosity. To overcome this limitation gel spinning is employed to produce fibres but this comes at a price. The gel spinning process requires extra chemical as solvent for the polymer. Lesser the amount of the solvent used better would be the process economically. One of the studies on the role of the concentration on the fibres properties was conducted by Lemstra and Smith [61]. To understand the role of concentration they prepared two groups of samples, one with very low polymer concentration and the other with very high concentration. They argued that the fibres produced from low concentrations attain very high draw ratios, which in turn reduces the defects, and increases the mechanical properties of the fibres. Fibres produced from a concentrated solution consisting of 10-50% wt solvent could not achieve draw ratio of more than 5:1, which is similar to the draw ratio achieved by melt spun polyethylene. They explained that this is due to the very high viscosity of the polymer and very long polymer chain length which does not allow the movement of the polymer during the extrusion process and leaves many defects in the structure of the fibre. Most prominent of them is grain boundaries which cause fracture upon drawing.

Lemstra and Smith argued that superior mechanical properties could only be achieved by preparing fibres from very low concentrations of polymer solutions. Prevorsek argued against it. He explained that the set of experiments he had conducted in Allied-Signal contradicted Lemstra's arguments. Their experiment showed an increasing trend in the strength of fibres with increasing polymer concentration as shown in Figure 2.28.

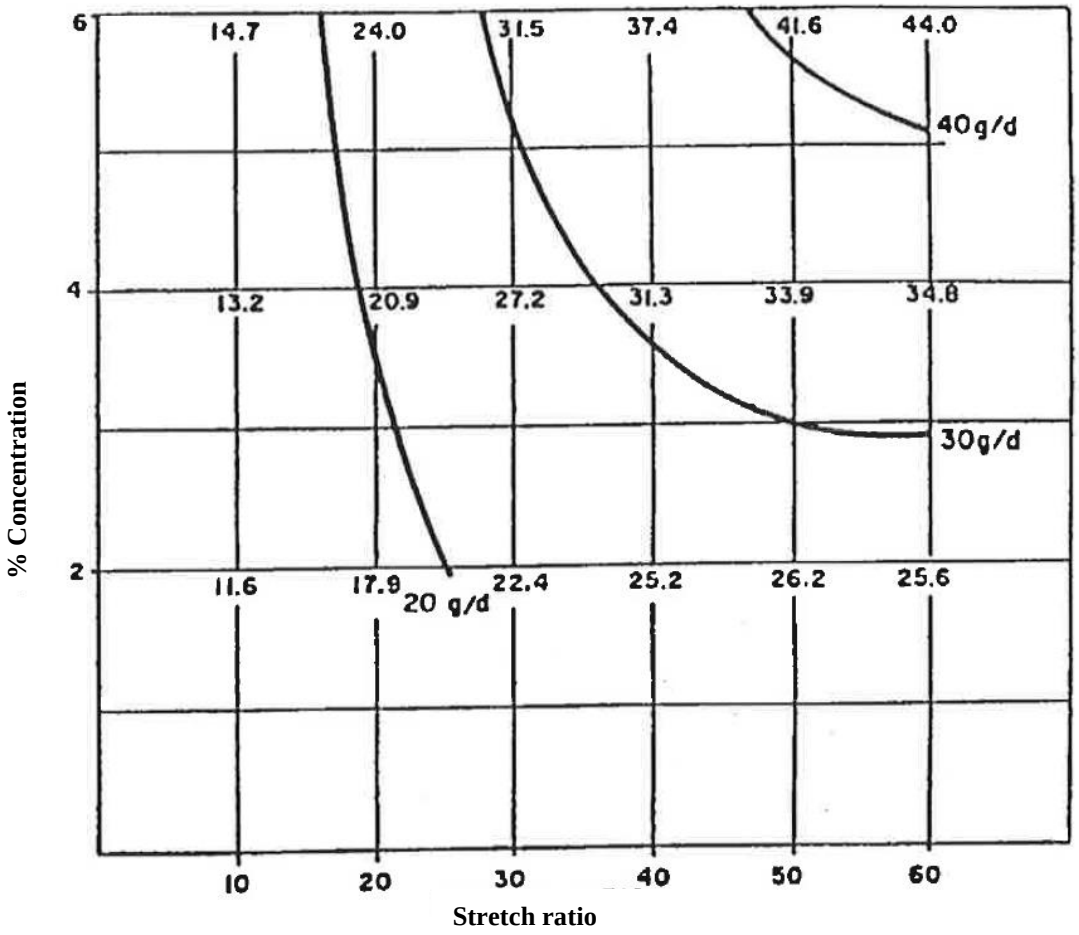

Figure 2.28 Relationship between concentration, draw ratio and strength [43]

He also argued that the precursor fibres showing high drawability and had no to very little porosity. However, it was claimed that to achieve a very high draw ratio, fibre should have a high level of porosity. He also claimed that in the concentrations covered by experiments 2-7%, the strength of the fibre increases with increasing concentration. Prevorsek's experiments contradicted the previous works. This indicated the possibility of a batter economical process for the production of UHMWPE fibres. Prevorsek further explained that the draw ratio of the product obtained by removing the solvent from gel is dependent on the morphology of the intermediate product. Since the strength of the fibre correlates with the maximum draw ratio, the

correlations regarding draw ratio are also applicable to strength. The morphology of the intermediate solvent free product relies on the concentration of polymer in the solution before the gelation. It also depends on the conditions under which gelation and crystallization occur i.e. cooling rate, tension, solvent and longitudinal and shear flow. It explains why Smith and Lemstra [61] found that the stretchablility of gel is inversely proportional to the concentration while Kavesh and Prevorsek [49] reported completely contrasting results. It explains that the crystallization conditions can reverse the trends in concentration dependence at some concentration levels. It was concluded by Prevorsek that the hypothesis that the entanglement state that exist in the solution largely remains unchanged during the formation of crystalline gels and is not supported by the rheology or the melts obtained on molten fibres or by the melt rheology of the un-oriented gels isolated from solutions. Furthermore, he concluded that the interference based on solution concentrations and extensibility (draw ratio) reported by Smith and Lemstra [61] should be regarded as a special case.

2.7.2.5 Drawing

Mechanical properties of the fibres from flexible polymers are much lower than the estimated for an ideal uniaxial extended chain structure (see Figure 2.7). It is not possible to achieve an ideal fibre structure due to the presence of long polymer molecule folds during crystallization [18, 19]. It is possible to reduce the number of chain folds by stretching but they cannot be completely eliminated. The fibre structures proposed by Fischer and Goddar [21] and Clark and Scott [20] are shown in Figure 2.8. The fibre structure model proposed by them also contains chain folds. Fibre drawing is an essential step contributing to fibre modulus, strength and dimensional stability.

Polyethylene has a unique ability to stretch the microfibrils though chain unfolding, which makes the microfibrils stronger through the formation of intrafibrillar tie molecules. These intrafibrillar tie molecules also exist in other fibres such as PET and nylon. However, stretching and strengthening of mircrofibrillar through formation of interfibrillar tie molecules are more significant in polyethylene than other fibres. Polyethylene is a unique case due to weak intermolecular forces and very strong primary bonds. The short repeating unit in polyethylene allows the formation of low energy crystal defects, which can easily be activated under applied stress at moderate temperatures, which allow the easy lateral displacement of polymer chains. Alternatively, these conditions do not exist in the case of PET, polyvinyl alcohol (PVA)

and nylon, where the lowest energy required to break the weakest molecule is only about 60% of the breaking energy of C-C bonds and the presence of longer repeating units and higher cohesive energies prevents the formation of low energy defects. Hence, the microfibrillar stretching and draw ratio of PE is much higher than any other polymer. The stretching in nylon and PET is the result of microfibril slippage which results in the formation of tie molecule [4].

The modulus of polyethylene fibres approaches the theoretical limit for a perfectly aligned flawless crystal under high deformation rates. The schemes of polyethylene solution during gel spinning are show in Figure 2.29. Figure 2.29(a) shows the pulling of the bundles of molecules out of the clusters of unoriented molecules. The entanglements migrates towards the clusters of unoriented molecules due to the stretching as shown in Figure 2.29(b). This migration results in anisotropic structure as shown in Figure 2.29(c).

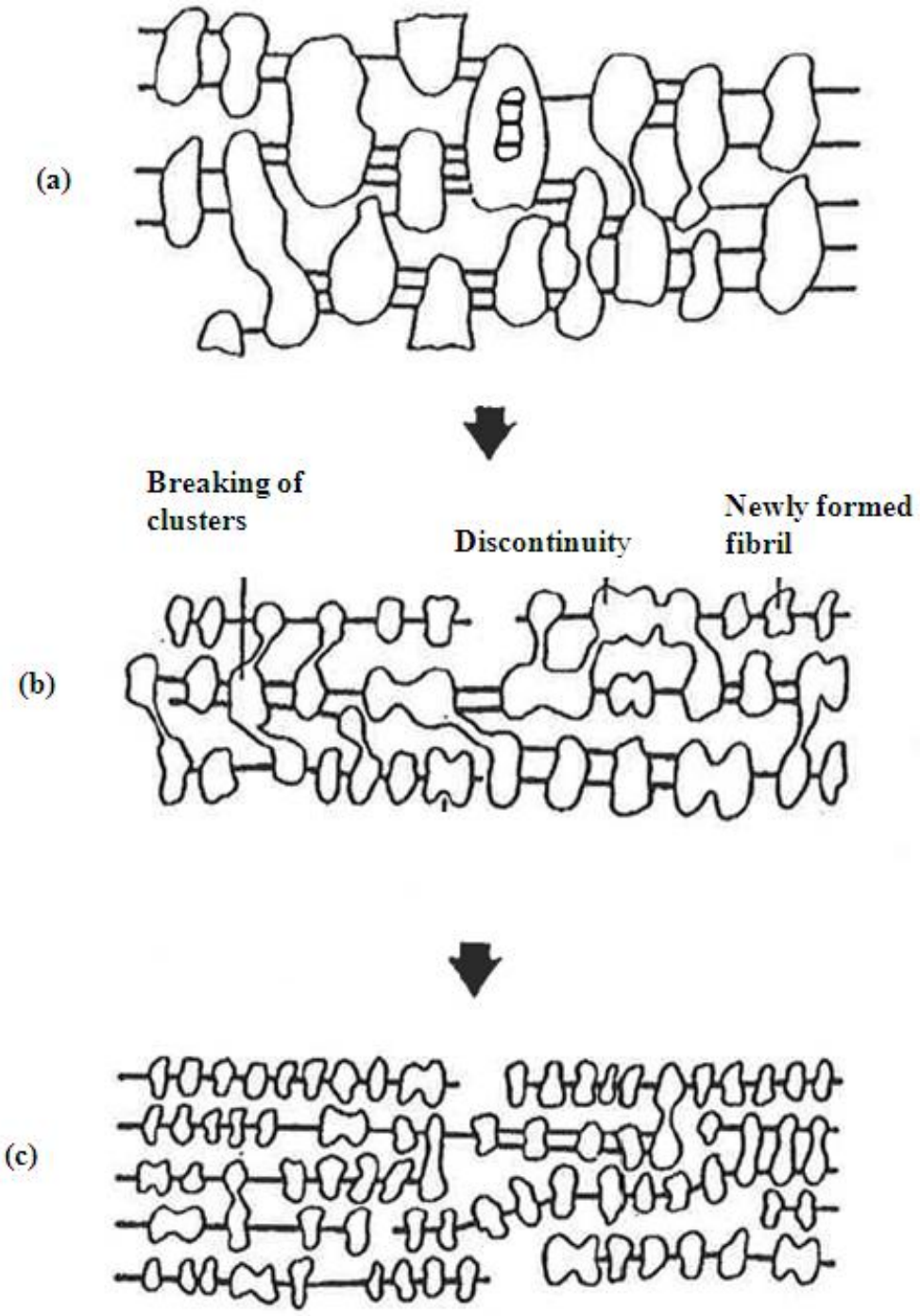

Figure 2.29 Flow schemes of polyethylene solutions during gel spinning [4]

Figure 2.30 shows a schematic mechanism of drawing proposed by Pennings and Smoook. It shows, at temperature between 100-130^{o}C the polymer chains are not very mobile, hence not aligning well. In the temperature range of 133-143^{o}C the mobility of the polymer chains increase a little allowing the chains to alight a little

better than the previous. While with the increase of the temperature in the range of 143-150^{o}C, the mobility of the polymer increases significantly which allows the polymers to align them along the fibre axis. This alignment of polymers chains bring the polymer chains closer to each other which gives rise to the Van der Waals' forces resulting in stronger fibres.

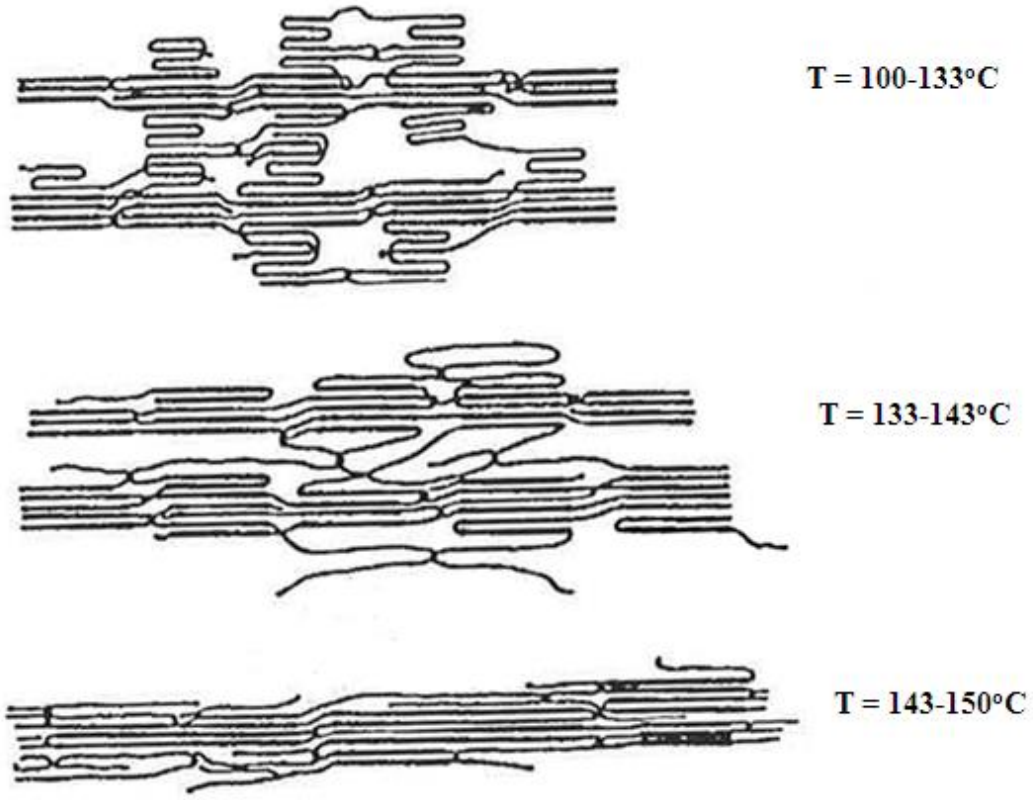

Figure 2.30 Deformation mechanism during hot drawing proposed by Pennings and Smook [8]

Drawing is the most studied process. At room temperature the natural draw ratio of most linear polymers is in the range of 5:1 to 10:1 [31]. A draw ratio of 20:1 was achieved by Clark and Scott, Firstly they drew the UHMWPE fibre to its natural draw ratio and then the fibres were slowly drawn to final draw ratio [20].

Capaccio and Crompton were able to achieve a high draw ratio at 115^{o}C. They investigated the temperature boundaries for effective drawing and were able to draw samples to 17:1. The effect of drawing on the stress strain curves is shown in the Figure 2.31. The samples drawn to a higher ratio demonstrate significantly higher strength

than the fibres drawn to a lower ratio irrespective of the molecular weight of the polymer.

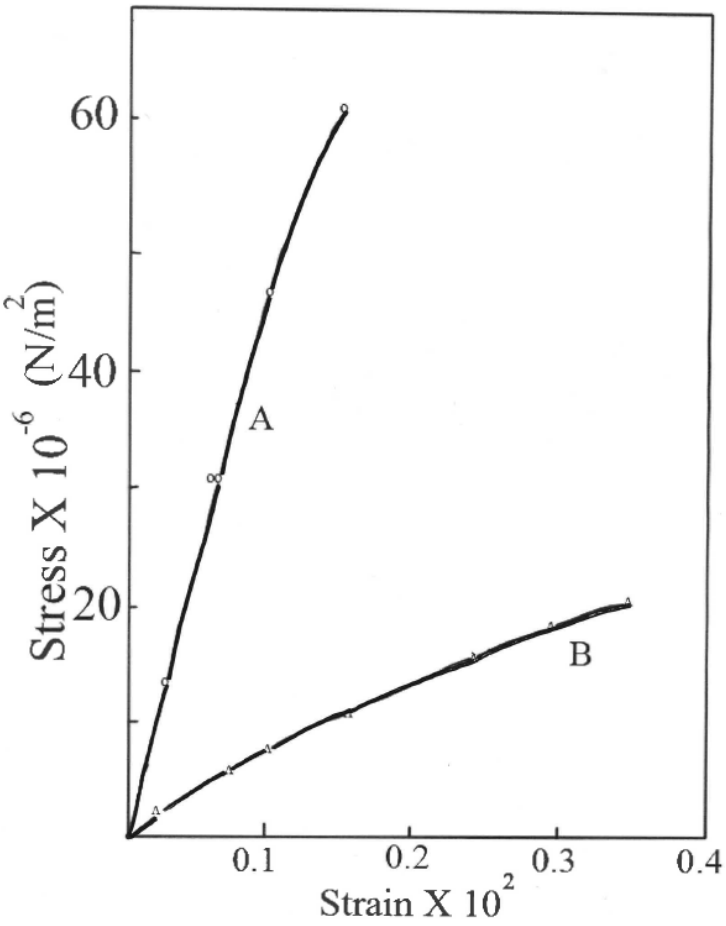

Figure 2.31 Stress strain curves of highly drawn (A) Linea polyethylene λ = 34 and (B) UHMWPE λ=17

The effects of different draw temperatures on strength and modulus of the fibre was investigated by Chen et al. [54]. They concluded that the modulus of the fibres increases with the increasing drawing temperature, indicating the increased energy consumed in fibre extension. Hence, the polymers become more and more coherent, thus increasing fibre draw-ability. Further they suggested that the strength of the fibre is not temperature but draw ratio dependent. A linear relationship between draw ratio and strength was reported by them same findings were reported by other researchers [51, 76]. They also indicated the relation between maximum draw ratio achievable and temperature. UHMWPE fibres were drawn to 50:1 at 150^{o}C and up to 32:1 at 100^{o}C but fibres could only be drawn to 16:1 at 25^{o}C, indicating a linear relationship between draw ratio and temperature. Pennings et al. also reported the increase of drawability with the increase in temperature up to 150^{o}C when they reported a draw ratio of 100:1 at

150^{o}C with fibres demonstrating high strength of 3.4GPa. The further increase in the temperature above 150^{o}C reduced the tensile properties.

The relationship between draw ratio and the concentration of polymer solution was studied by Smith and Lemstra [61]. They concluded that the lower concentration allows fibres to be drawn to higher ratios. Their high concentrated samples did not show any significant increase in the maximum draw ration over the melt spun fibres. They argued that the quenching of dilute polymer solutions at room temperature increases the fixation of the network structure because of the crystallites acting as physical cross-links. During the subsequent hot drawing, temporarily anchored molecules in these crystallites are stretched which prevents the relaxation of the polymer molecules in the drawing process by delaying the dissolution or melting of the crystallites. Removal of the solvent from gel structure before drawing did not appear to have any significant effect on the intermolecular topology. Other researchers also reported the same inverse relationship between concentration and draw ratio. They argued that this is due to the reduced number of entanglements per molecule in solution-spun polymers in comparison to melt-spun fibres [50, 51, 77-79]. The same phenomenon is also attributed to the ultra-drawing of single crystal mats [80-82]. Prevorsek argued against this [4]. He explained that the set of experiments conducted in Allied-Signal contradict arguments of an inverse relationship between concentration and draw ratio. The experiment showed an increasing trend in the draw ratio of fibres with increasing polymer concentration as shown in Figure 2.28.

He also argued that the precursor fibres showing high drawability had no to very little porosity. However it was claimed that for achieving very high draw ratio, fibre should have a high level of porosity [71]. He also claimed the concentration covered by their experiments (2-7%) , the strength of the fibre increases with increasing concentration [4].

2.7.2.6 Environmental and Health Risks of Gel spinning Process

Gel spinning process depends primarily on the use of a hydrocarbon solvent which allows the extrusion of the UHMWPE into fibres this solvent then needs to be removed. The removal of the solvent requires a secondary more volatile hydrocarbon solvent. A variety of solvents were utilised by different researchers each having adverse effect not only on the environment but also hazardous to the human expose to them. The paraffin was used most extensively by the different researchers [10, 55, 61, 71-73].

The paraffin has very low volatility but one of its component i.e. η-hexane is very volatile and hazardous chemical, hazards to human includes nausea, irregular heartbeat, headache, lung congestion, nerve damage, brain damage, blurred vision, impotence [83]. The second most widely reported solvent was decalin [39, 50-52]. Decalin being a petroleum product is unsustainable, its volatile nature makes it an occupational hazard it is a known respiratory irritant. Studies on rats have shown the carcinogenicity of the decalin [84]. The other chemicals used as solvent includes dodecane, kerosene and p-xylene. These solvents are also derived from the petroleum thus are not sustainable apart from sustainability the health hazards of these chemical are another concern. The hazards include lung damage, central nervous system damage, carcinogenicity [85-87]. The problems become two folds when the second solvent is used to extract the spinning solvent these extraction solvents includes hexane, tricholoro-trifloroethane (TCTFE), xylene etc. These chemicals are very hazardous to humans and environment the risks to human involves e.g cancer, nephropathy, lung damage, central nervous system damage, kidney damage, liver damage while due to their toxicity to aquatic life, high mobility in soil which results contamination of ground water and inability to biodegrade they are an environment concern [86-94]

2.7.3 Polymer Blends

Polymer blending is a process in which two or more than two polymer are mixed together and extruded as one fibre. Blending is a very useful technique to alter the mechanical property of fibre by using different blends. Vikash reported the dependence of the tensile properties of the fibres on the blending percentage of the polymer [95]. Blends of UHMWPE were studied by Sawatri et al. [63]. They produced the blends by gelation/crystallization from solution. The blends were produced in different percentages i.e. 75/25, 50/50 and 25/75. The blend fibres produced were drawn to ×50, which is very high for PP. The high draw ratio indicated the intimate mixing of UHMWPE and PP. Sawatari and Matsuo studied the blends of UHMWPE and LMWPE (low molecular weight polyethylene) produced by gelation/crystallization [62]. The blends of UHMWPE/LMWPE with concentration percentage of 100/0, 91/9, 67/33, 50/50, 0/100 were studied. Their DSC results showed two peaks. The peaks on higher and lower sides were associated with melting point of UHMWPE and LMWPE crystallites respectively. The peaks shifted towards the higher temperature due to the presence of UHMWPE while the peaks shifted towards lower temperature due to LMWPE as shown in Figure 2.32. Drawing of the blends showed an interesting

phenomenon the peaks at lower temperature due to the LMWPE crystallite completely disappeared in the blends 91/9 and 67/33, while in the 50/50 blend peak became extremely small as shown in Figure 2.33. They proposed it could be due to growth of LMWPE crystallites and/or a decrease in the number of defects with crystallites which cause a peak shift towards higher temperature.

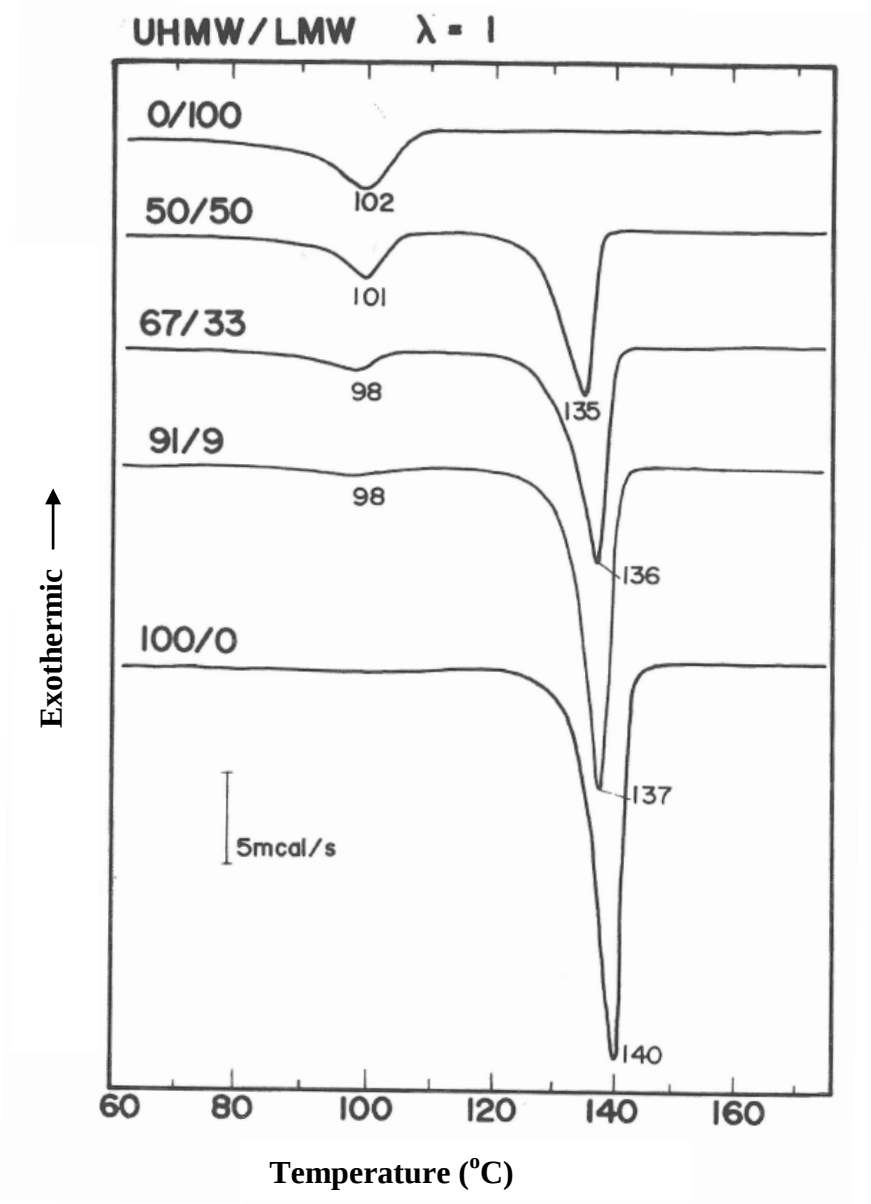

Figure 2.32 DSC curves of undrawn blends (100/0, 91/9, 67/33, 50/50, and 0/100) [62]

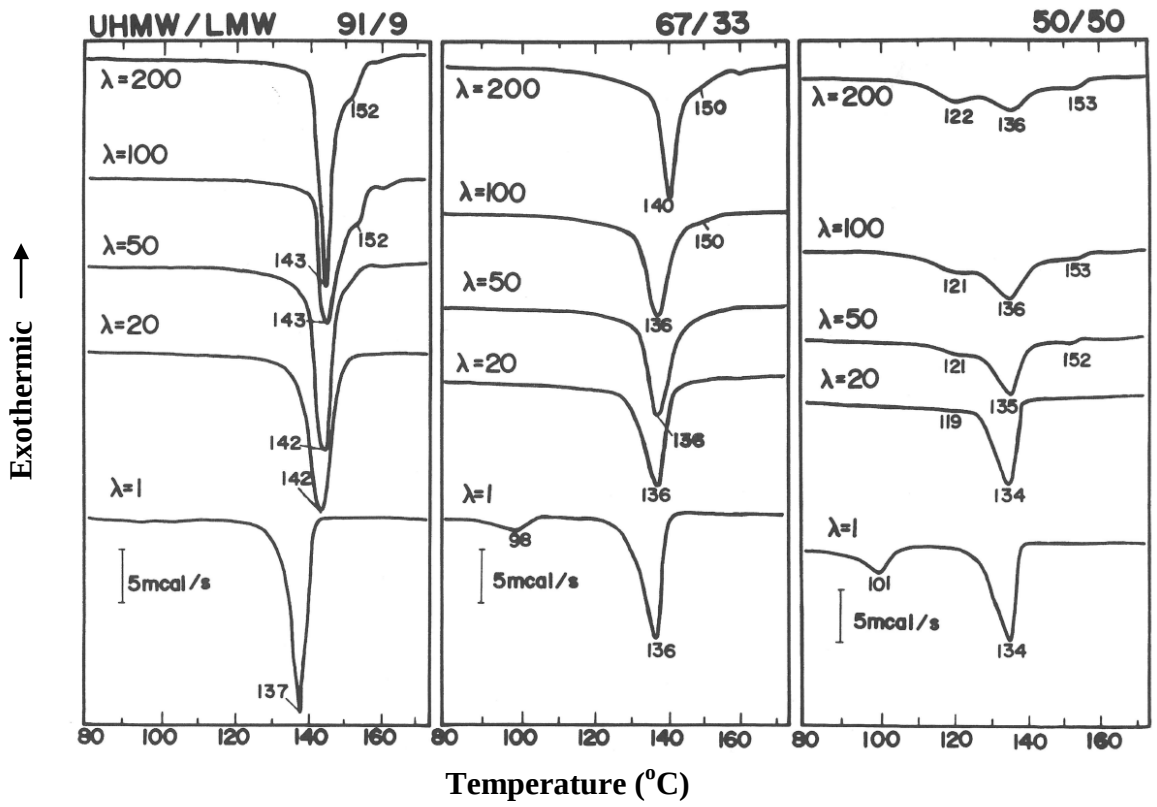

Figure 2.33 DSC curves of the blends (91/9, 67/33 and 50/50) drawn to various draw ratios λ [62]

2.8 Potential Natural Alternative Solvents

Solvents used to produce UHMWPE fibres are hydrocarbons of various structures e.g. paraffin, kerosene, dodecane, decalin etc. Since, there has been a wide variety of hydrocarbon solvents successfully used to produce UHMWPE. The most appropriate environmentally friendly solvent to replace these petroleum solvent are natural hydrocarbon solvents such as natural oils. Since the UHMWPE polymer powder dissolves at 130°C. The oils should be able to remain stable at temperature above 130°C.

2.8.1 Sunflower Oil

Sunflower oil is natural oil with a flash point of 316°C, smoke point 209°C and fire point of 341°C thus it is very stable at temperatures around 130°C. The sunflower oil contains 98-99% triacylglycerols and a very small fraction of phospholipids, tocopherols, sterols and waxes [96]. The triacylglycerols structure is shown in the Figure 2.34 the presence of very large number of hydrocarbons in the structure of triacylglycerols makes the sunflower oil a potential alternative as a solvent in place of hydrocarbons derived from the petroleum [97]. The presence of tocopherols, which are

natural antioxidant can prove useful to avoid degradation of polymer during dissolution by avoiding oxidation.

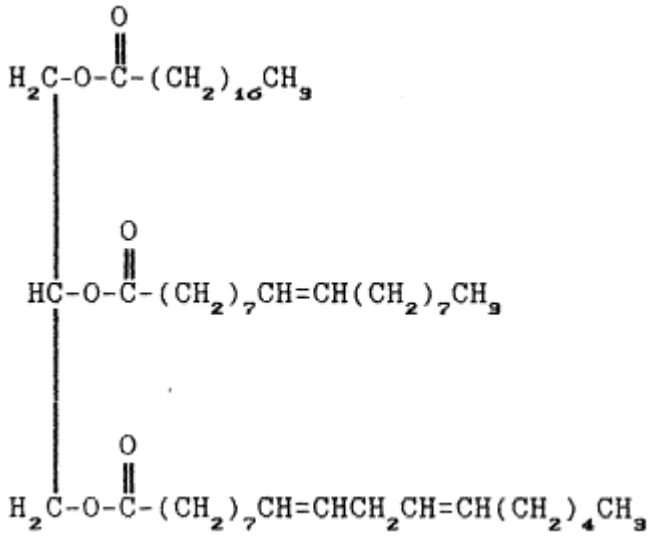

Figure 2.34 Structure of a typical triacylglycerols [97]

2.8.2 Palm Oil

Palm oil is cheaper than sunflower oil. It also contains 95% of triacylglycerols with traces of other constituents e.g. phosphatides, sterols, tocopherols, tocotrienols, etc. Palm oil is very stable at temperatures exceeding 130^{o}C. The presence of very long chains of hydrocarbons in triacylglycerols makes it highly non polar thus a potential candidate to be used as solvent for UHMWPE.

2.8.3 Orange Terpene

Orange terpene is a biodegradable natural hydrocarbon occurring in orange peel. It has been used in diverse chemical applications due to its positive environmental profile and pleasant orange aroma. The orange terpene is widely used as a cleaning solvent replacing hazardous petrochemicals. Orange terpene has been the status of GRAS (generally recognised as safe) by FDA (food and drug administration of United States). Orange terpene is not considered a carcinogen, a developmental toxicant or mutagenic [98]. Terpene is natural hydrocarbon with carbon skeleton composed of isoprene C_5 unit (CH_2=C(CH_3)-CH=CH_2). The non-toxic and biodegradable nature combined with the presence of hydrocarbon makes it a potential alternative to petroleum hydrocarbons.

2.9 Ultrasound in Polymer Chemistry

High-frequency sound waves are called ultrasound. Depending on the frequency they are divided into two types destructive (20 kHz to 2 MHz) and non-destructive (5 MHz to 10 MHz). The non-destructive ultrasounds are used for diagnostic purposes while the destructive ultrasounds are used for sono-chemical applications. When ultrasound is irradiated on a liquid it causes the liquid to compress and expand locally. The liquid follows the movement but the distance between the molecules become so large that the liquid is "broken". This creates the cavitation bubbles which increase in size during several compression and rarefaction cycles. After growing beyond certain size, it become unstable and collapses. This collapse causes the liquid surrounding the bubble strongly accelerates and the collision between the molecules creates hot spots with very high temperature and pressure. The high temperature induces the chemical reaction while the high pressure is responsible for the physical changes.

Ultrasound has been widely used to initiate the polymerization and polymer scission. In the polymer scission the collapse of cavitation bubbles induces strong shear gradient in addition to hot spots. The effects of hot spots are very local but the mechanical effects take place over longer distances (micrometer). This causes the extension of the larger molecules and even scission. But this scission can be avoided by using a viscous polymer solution [99]. The increase in the viscosity slows down the creation of the cavitaiton bubbles thus avoiding polymer scission but allows the extension of the polymer [100].

2.10 Fabric Coatings

Coating is a process in which a layer is deposited over the fabric. There are many coating techniques. The main purpose of all coating techniques is to control the amount of the add-on resin and preserve the properties of the fabric. The control of the resin add-on is important in fabric coating. Resins solid contents and viscosity are main parameters, which are used to control resin add-on. The properties of the solution are the most important parameter in coating. If the concentration of the solid contents is too high, the polymer coating solution does not adhere to the substrate. Very low concentration solutions result in very thin coating. Hence, the properties of the polymer solution plays a vital role in the coating process [101]. Since the gel spinning of UHMWPE also depends on the properties of the polymer solution. Hence, parameters that affect the properties of polymer solution such as temperature of dissolution, phase

separation temperature, concentration of the polymer etc all are equally important for both gel spinning and coating.

The coating thickness is also controlled by controlling the amount of add-on. There are different mechanisms, which are used to control the add-on. Knife on air as shown in Figure 2.35 is one of such mechanism to control the thickness of the coating. In knife on air design fabric is kept in tension and passed under the knife. The gap between the knife and the fabric controls the amount of add on. In this design the fabric tension plays vital role thus delicate fabrics which do not have sufficient strength to resist the physical changes under high tension cannot be coated using this method. Flexible fabrics are another class which are difficult to coat with this method.

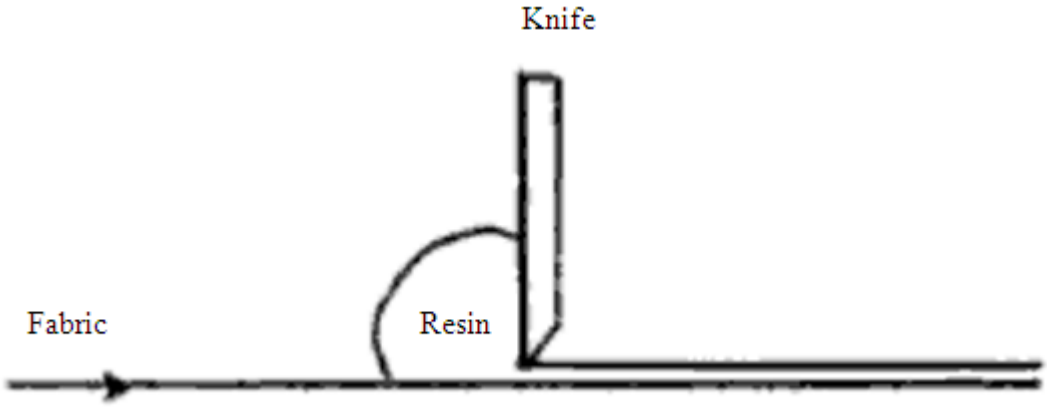

Figure 2.35 Knife on air [102]

In contrast to knife on air design where no base is present for the fabric in the two designs shown in Figure 2.36 and Figure 2.37 the fabric is provided a base in the form of table or blanket these two designs provide better uniformity than the knife on air design in the application of add-on. Unlike the knife on air design these two designs do not rely on the tension of the fabric due to the presence of base which keeps the fabric stable allowing the coating of the delicate and flexible fabrics.

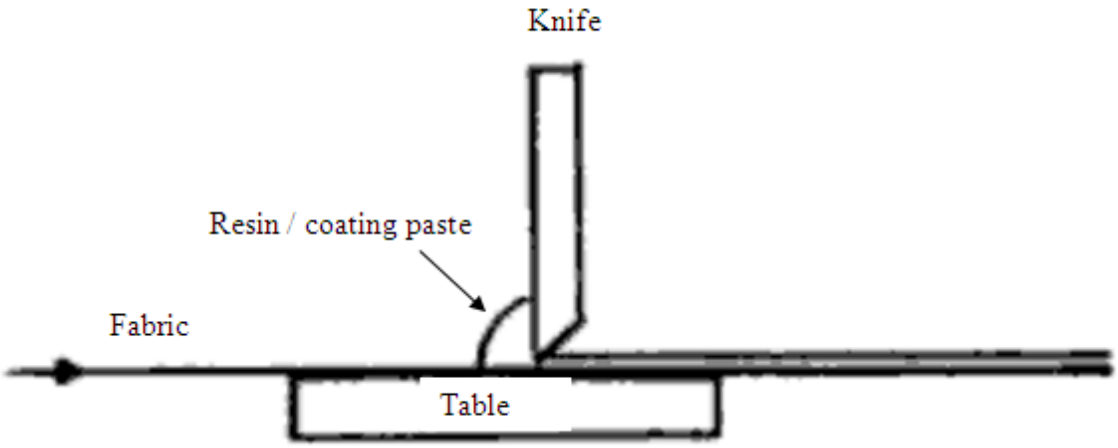

Figure 2.36 Knife over table [102]

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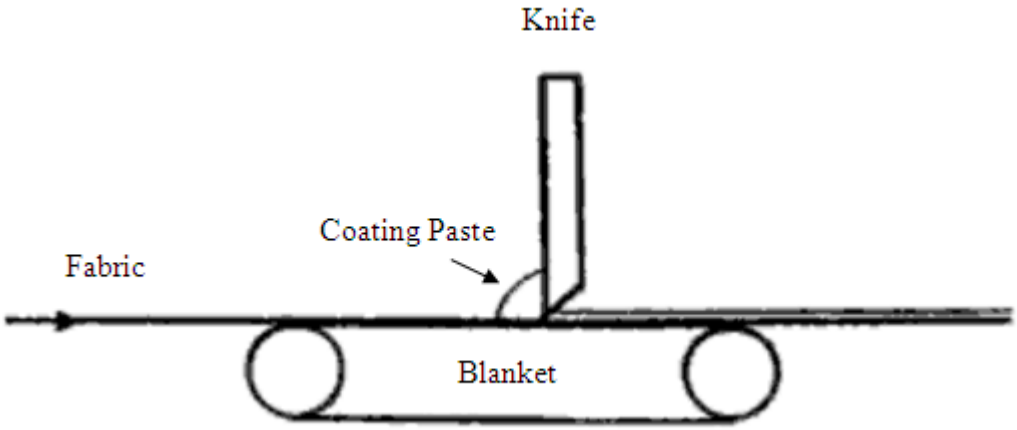


Figure 2.37 Knife over blanket [102]

Although machine characteristics and geometry play an important role in controlling resin add on in knife based coating mechanisms the resin add-on is also controlled by different blade profiles as shown in Figure 2.38, blade angle and gap separation of the blade over the coating table.

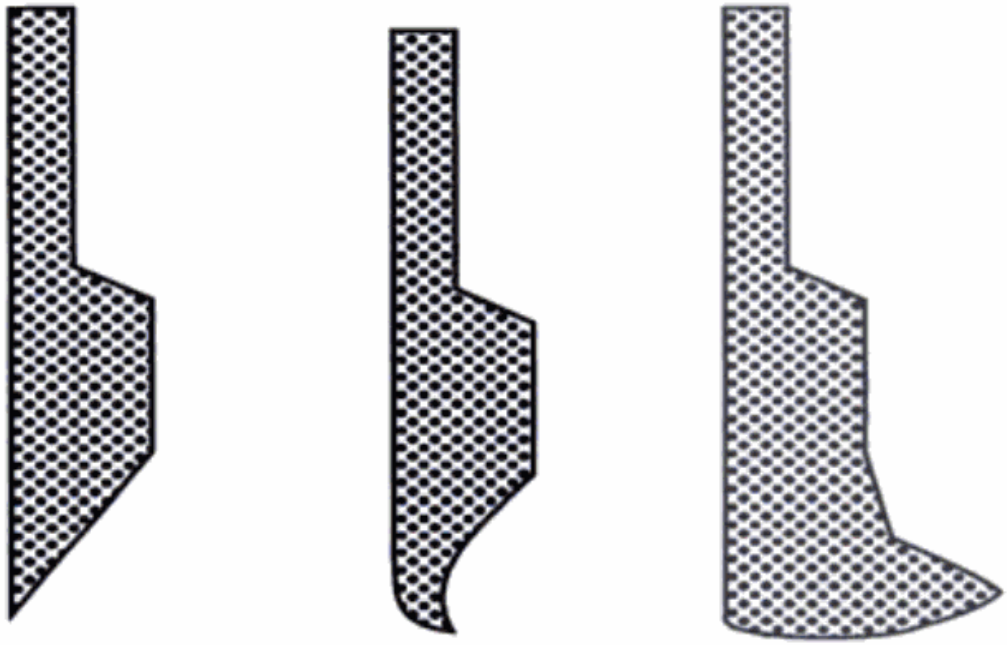


Figure 2.38 Different profiles of the knife [102]

Another category of coating methods utilises of the rollers to control resin add on. Roller methods use the gap between the rollers, speed of the rollers and contact angle to control the add-on example of such mechanism are shown in Figure 2.39 and Figure 2.40. In the roller on roller nip coating design shown in Figure 2.39 a small part of bottom roller is kept immersed in coating paste. The rotation of the bottom roller carries some coating past with it that comes in contact with the fabric which is passed through the nipping point. The nipping point removes the excess amount of past and provides a uniform resin add on.

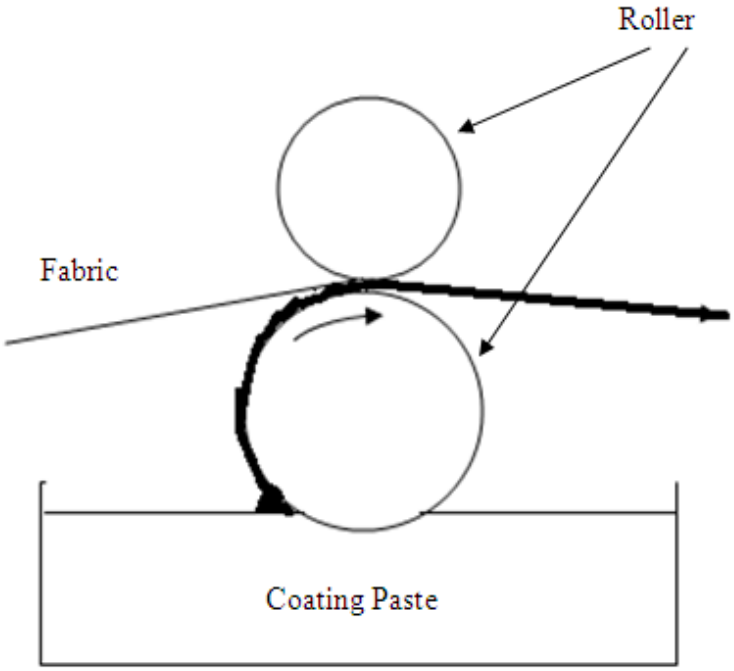


Figure 2.39 Roller over roller nip coater

Calander coater consists of three rollers two of which works as feeding rollers which control the amount of coating past conveyed to the fabric. While the third roller in combination with one of the feed roller provides the nipping point which controls add on amount.

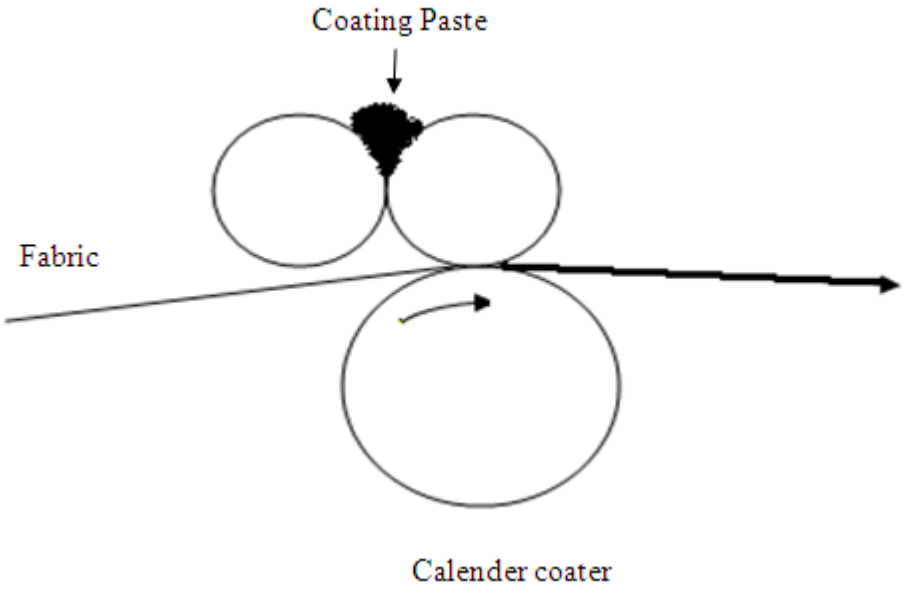


Figure 2.40 Schematic of Calender coater

Blade on roller is another method of coating shown in Figure 2.41. It is a combination of both knife and roller coating design for precise control of resin add on. The design consists of a roller and knife. The fabric is passed between the roller and the knife. The gap between the blade and the roller is used for the more accurate add-on control. The blade scrapes off the access amount of resin hence providing better control over the resin add-on. The speed of the roller can also be controlled which provides more precise control over the add on [103].

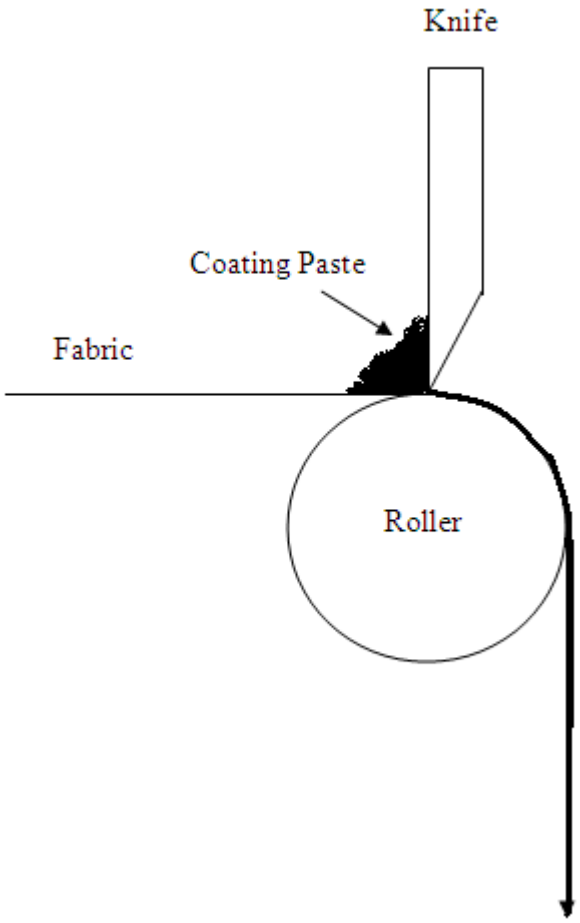


Figure 2.41 Schematic of knife over roller coater

2.11 Summary

The relevant literature has been reviews which provided the understanding of the UHMWPE on chemical and physical level. Different processes for the production of UHMWPE fibres were reviewed. Gel spinning process which is the widely reported process has been reviewed which contains, extrusion techniques, solvents used, solvent

extraction methods, polymer concentration, drawing and the environmental and health risks. The review of the spinning processes of UHMWPE pointed out the environmental and health risks associated with the solvents used in the processes.

The spinning process reported by different researchers utilises petrochemicals to extrude the fibres. These solvents are then extracted by utilising other more volatile solvents. The solvent used in the gel spinning are all petrochemicals thus not sustainable. These solvents also raise an environmental concern by being hazardous to aquatic life. Their high mobility in the soil carries the risk of contaminating the ground water. These solvent also carries health risk to human that includes cancer, lung damage, central nervous system damage, kidney damage, liver damage etc.

The blends of the UHMWPE with other polymers reported in literature by gelation/crystallization showed improvement in the strength of the blend fibres. However, there was no literature available on the effect of blending by melt spinning. The blending of UHMWPE with other polymers can prove useful in improving the strength of the blend fibres, which can lead to a solvent free melt spinning process.

The natural oils such as palm, sunflower and terpene have similar chemical properties to the solvents used in gel spinning of UHMWPE. Since the natural oils are from the natural plants thus they are sustainable. These oils are also not dangerous to environments hence does not have special govt regulations to dispose. Their ability to biodegrade is another positive point since they do not need extra treatment to dispose. Since these oils are either edible (sunflower and palm oil) or generally recognised as safe (terpene), they do not carry any health hazards to the people working with them improving the working environment.

One of the problems in the extrusion of UHMWPE fibres is the high number of entanglements due to their very high molecular weight. In the past ultrasound had been used for the polymer scission. Same phenomenon can be used to disentangle the polymer chains.

The superior properties of UHMWPE can prove useful as coating on fabrics in the wide variety of application such as shade material, irrigation systems, pond liners, hoses, bags, seed/crop covers, fencing, bulk containers etc in agriculture industry. While in construction industry it could be used as safety fencing, wind covers, concrete curing, safety vests, hoses, conveyer belts, truck covers, drainage ditches, architectural

structures etc. In the clothing industry coatings could be used in shoe uppers and linings, artificial leathers, rain wears, garment linings, backing stiffeners, water replants, stain repellents etc. Both coating and gel spinning process depends on the properties of the polymer solutions. Understanding of the factors, which affects the properties of the solution, is important for both gel spinning and coating which can lead to develop a process for the coating of UHMWPE.

This chapter provided the foundation for this research. The following chapter describes the methodology formulated to achieve the objectives of the research. The next chapter also contains the information about the instruments, methods and material used in this research.

Chapter 3 **Materials and Methods**

3.1 Introduction

The previous literature review chapter provided the foundation of the research. Problems and potential solutions were reviewed. This chapter presents the methodology adopted to address the problems and to achieve the set objectives. The materials used in this research and their properties are also discussed. The working principle of the machines and the methods used for the preparation of the fibres and the coating are explained in detail. The chapter also contains the description of the testing instruments used in this research.

3.2 Methodology

The literature review provided the understanding to plan the research in order to achieve the objectives described in the section 1.4. The research methodology contains two parts first part addresses the problems associated with the production of UHMWPE fibres while the second part addresses the coating of UHMWPE.

3.2.1 Fibres

A two pronged approach would be adopted to find an environmentally friendly process for the production of UHMWPE fibres. In the first approach, the blends would be prepared to find a solvent free process, while the second approach investigates the natural solvents for the preparation of UHMWPE fibres from gel spinning.

The first approach involves the preparation of UHMWPE blends by melt spinning. The polymer blends has been widely used in the past to achieve the fibres with a wide range of properties. The blends of UHMWPE with other polymers prepared by gelation/crystallization from solution have been reported in the past. However, in the present research the blends of the UHMWPE with polypropylene and polyethylene would be prepared by melt spinning. The successful preparation of the blends from melt extrusion would lead to find a complete solvent free process for the preparation of the UHMWPE. The preparation of UHMWPE blends would lead to a series of experiments to find the maximum percentage of UHMWPE with which blends could be made, which could result in a solvent free process for the production of UHMWPE blends with very high percentage of UHMWPE.

The second approach involves the investigation of the natural solvent as alternative to petrochemicals. The naturally occurring chemicals having similar chemical properties would be used to prepare the UHMWPE gel. After finding the suitable solvent the gel would be extruded on standard ram extruder to form the gel fibres. The gel fibres contain both UHMWPE and spinning solvent the removal of the solvent is very necessary to get dry fibres. Since one of the objectives was the elimination of the solvent removal solvent the removal of the spinning solvent without utilisation of any additional solvents would be investigated. Once the dried fibres have been achieved from ram extruder, an appropriate experimental design will be carried out to identify the factors which plays vital role in the strength of the fibres. After implementing the experimental design and finding the conditions for the extrusion of UHMWPE, the gel spinning will also be carried out on screw extruder. One of the problems associated with the spinning of UHMWPE is the presence of very high number of entanglements. The ultrasound treatment will be applied to the gels to investigate their effect on the entanglement of the polymer chains.

3.2.2 Coating

A process will be developed to coat UHMWPE. The first step in the development of the coating would be to prepare the appropriate polymer solution. Solutions will be prepared with different percentages of polymer. Since the viscosity of the polymer solution plays a vital role in the coating, it will be investigated to find the optimum concentration of polymer solution. The standard methods of coating will be investigated to coat the polymer on the fabrics and also to understand the interaction of the polymer solution and fabric, which would lead to the development of a custom designed coating machine for the coating of UHMWPE.

3.3 Materials

Two grades of UHMWPE provided by Ticona UK under the name of GUR 2122 and GUR 4120 were used in the research. The properties of the polymers are shown in Table 3.1. Since extrusion of UHMWPE with higher molecular weight is more difficult than lower molecular weight polyethylene due to presence of high number of polymer entanglements due to very long polymer chains. The polymer grades were chosen due to their higher molecular weight than other grades. Orange terpene was acquired from Sigma-Alderich: boiling point 176^{o}C. Decalin also known as decahydronaphthalene with the boiling point 189 - 191^{o}C was acquired from Sigma-Alderich. Kerosene oil

used in this research was acquired from Sigma-Alderich. The Kerosene grade with boiling point of 175^{o}C was used in this research. Paraffin oil was also acquired from Sigma-Alderich.

	GUR 2122	**GUR 4120**
Density	930kg/m^3	930kg/m^3
Average molecular weight	4.5×10^6 g/mol	5×10^6 g/ml
Melt flow index	<1 g/10min	<0.1 g/10min
Melting point	130-135 ^{o}C	130-135 ^{o}C

Table 3.1 Properties of UHMWPE polymers

3.4 Differential Scanning Calorimeter

Differential scanning calorimetry (DSC) is a technique to measure the thermal properties of the polymers by measuring the amount of heat absorbed by the polymer relative to a reference material as shown in Figure 3.1. Materials exhibit change in enthalpy when going through a chemical or physical change. DSC takes advantage of these changes by measuring the change in enthalpy of the material to indicate phase changes corresponding to a particular temperature. DSC is widely used to find melting point, enthalpies of melting, crystallisation temperatures, glass transition temperatures and degradation temperature.

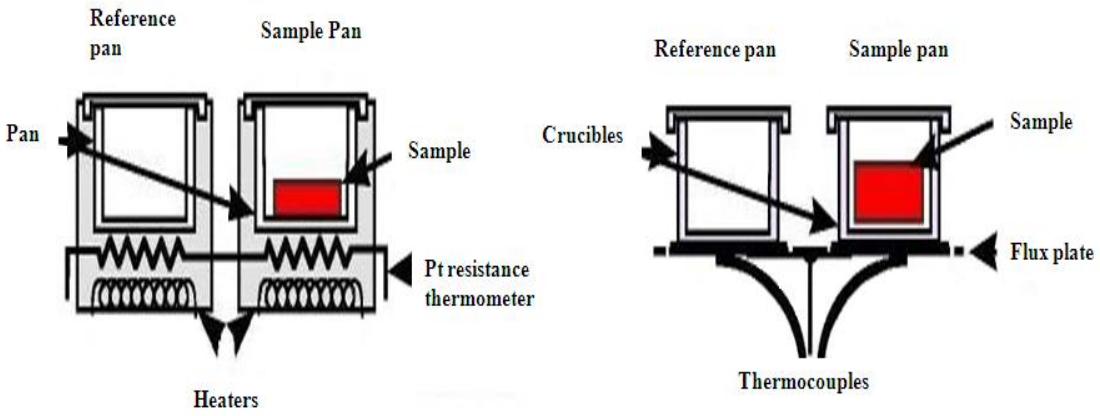


Figure 3.1 Schematic of DSC heating head [104]

The DSC consists of two heating units equipped with temperature sensors. The sample and the reference (empty pan) both are heated. During heating, both are maintained at same temperature. Since, the samples go through enthalpy change during different physical or chemical reactions e.g. phase change the sample emits or absorbs energy to remain at the same temperature as the reference. To maintain both sample and reference at same temperature, a computer is connected to the machine and various signals and software are used to decide where and how much heat to provide. This information is processed by the computer software and presented in the form of enthalpy against temperature graphs. A typical DSC graph is shown in Figure 3.2. In Figure 3.2 T_g indicates glass transition, T_c indicates crystallization peak and T_m represents melting point.

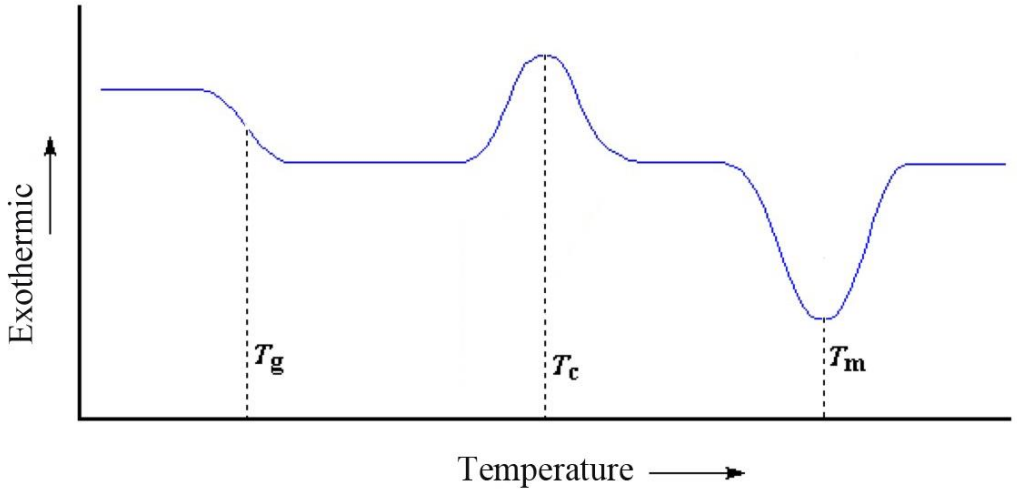


Figure 3.2 Typical example of a DSC curve [105]

In this work, samples of 7.0 mg were sealed in aluminium pans and their thermal properties measured by using a Mettler DSC 12E with TA89A software to record the data and control the heating. The instrument was calibrated using indium. All the scans were performed at $10^{o}C\ min^{-1}$.

3.5 Melt Flow Index

Melt flow index (MFI) is an important criterion to determine whether a polymer is extrude able. It is the mass of polymer in grams extruded in a standard time of 10 min at specific temperature. In this work MFI was measured by using Rayran Melt flow system model 5MBA. A schematic diagram of the instrument is shown in Figure 3.3 the instrument consists of a heated barrel with diameter of 9.57 mm with a capillary die having 2.09 mm hole diameter and length of 8 mm. The barrel is equipped with heater and thermocouple to control the temperature. The polymer was fed into the barrel and heated to the required 150 ^{o}C temperature for 5 min. The material was then forced through the capillary by placing a block of 2.16 kg over the piston. The extruding polymer is cut off after every 10 sec period. The MFI was calculated by measuring the mass of the polymer cut off extruded from the orifice by using the Equation 3.1. BS standard BS EN ISO 1133 was implemented to calculate the MFI.

$$\text{MFI} = \frac{600 \times m}{t} \tag{3.1}$$

where,

m = mass of the cut off in grams

t = time interval of cut off in sec

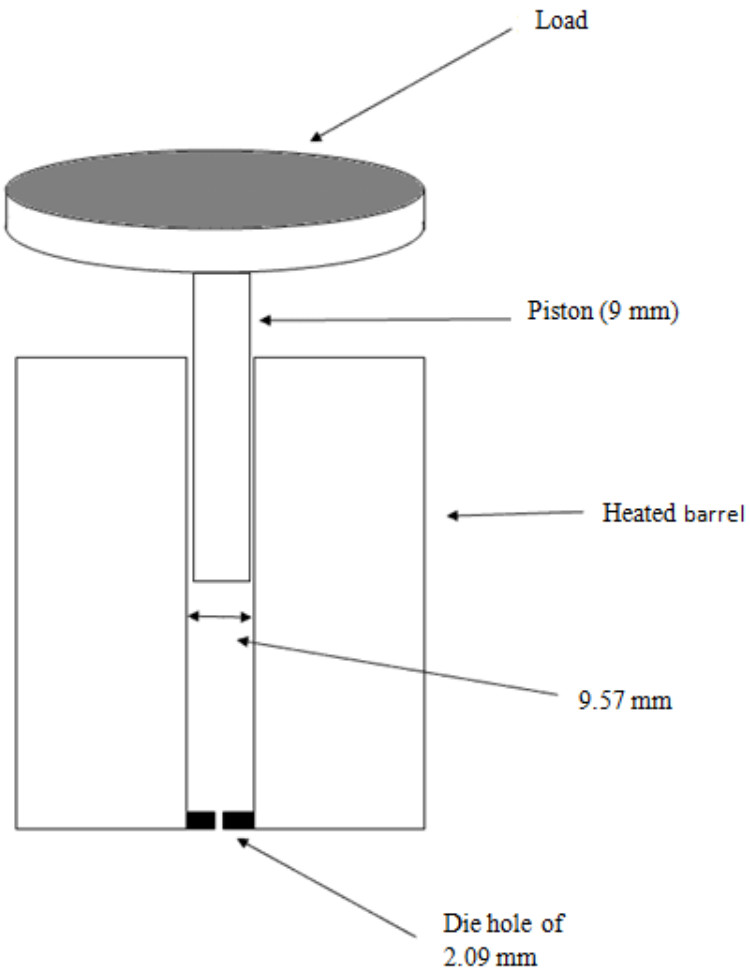


Figure 3.3 Systematic diagram of The MFI instrument

3.6 Extrusion

Extrusion was carried out using an ESL ram extruder with barrel inside diameter of 19 mm and barrel length of 15 mm. The ram had a diameter of 20 mm. Figure 3.4 shows the schematic diagram of ram extruder. The barrel contained a heater, temperature sensor and pressure sensor to control the process. The ram was capable of providing up to 700 Psi pressure. The extrusion was carried with a monofilament die having a hole diameter of 1 mm. The extruded fibres were quenched with a water bath at ambient temperature.

An ESL single screw extruder (model 250) with a screw of diameter 25 mm and L/D (length to diameter) ratio of 20:1 was also used for experimental purposes. The extruder contains three heating zones which could be controlled separately. The extrusion was carried out with a monofilament die. Extrudate was quenched in a water bath at

ambient temperature. The schematic diagram of the screw extruder is shown in Figure 3.5. Details of the individual experiments will be discussed in Chapter 4.

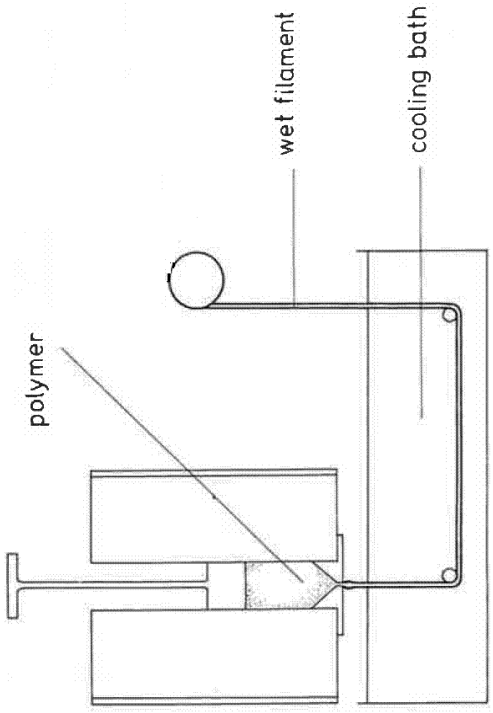


Figure 3.4 Schematic diagram of Ram Extruder [39]

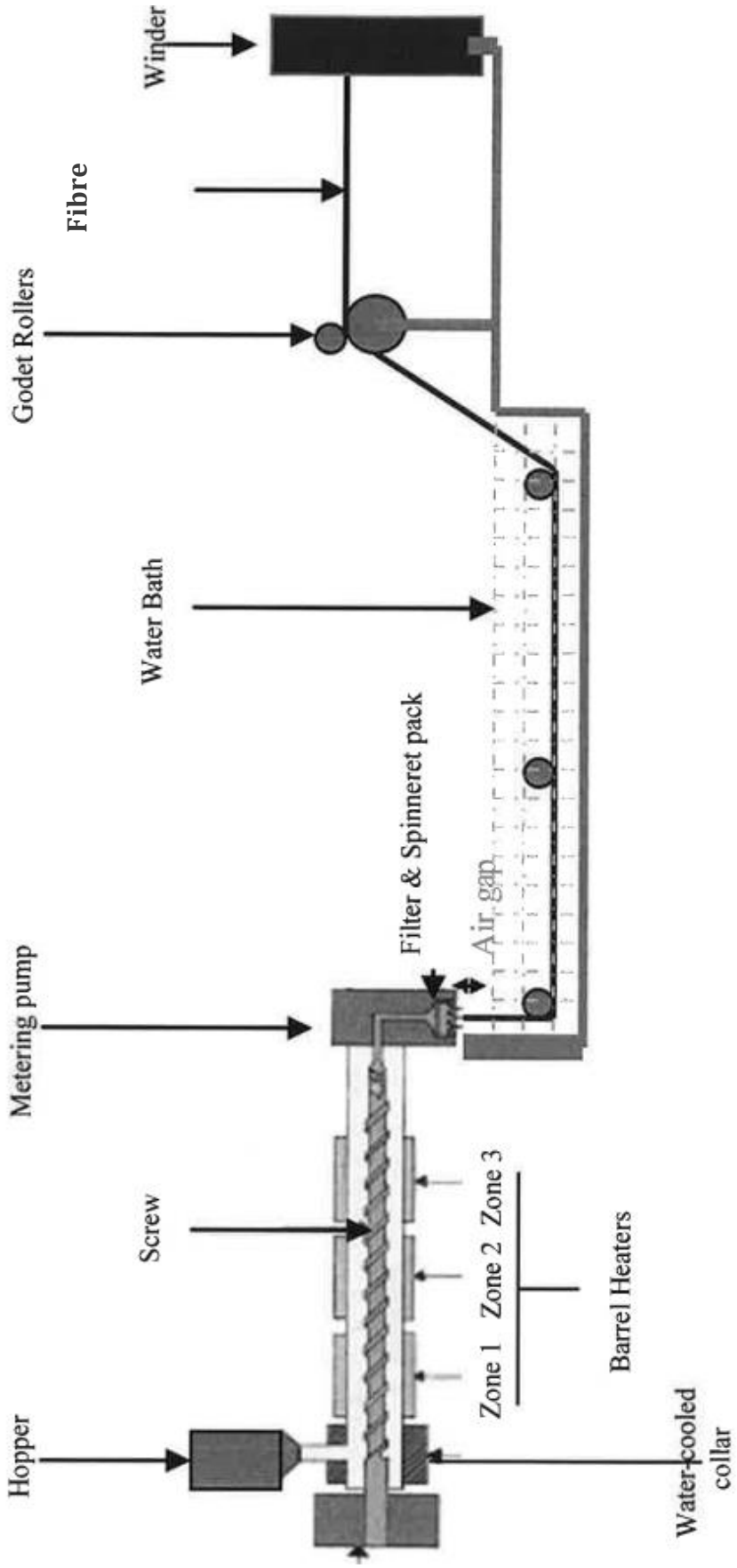
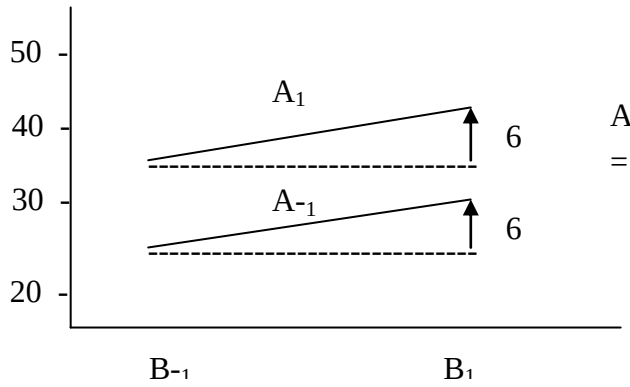


Figure 3.5 Systematic diagram of ESL Bench Extruder [95]

3.7 Experimental Design

Taguchi's method of statistical experimental design was used to identify the effect of different factors and interaction between various processing factors in order to understand the terpene based gel spinning process [106]. The interaction between two factors is measure of a factor behaving differently depending on the change in other factor. In order to find the interaction e.g. A and B, the effect of factor A at the high and low levels of factor B is calculated. The difference of these two effects is then divided by 2 to get the interaction effect of AB. Figure 3.6 shows an example of such calculation of interaction effect and geometric interpretation. In the Figure 3.6 -1s represents the low levels while 1s represents the high levels. At level -1 for factor A, changing factor B from level -1 to level 1 causes the response to increase from 25 to 31. At level 1 of factor A changing factor B from -1 to 1 causes the response to change from 36 to 42 in both cases the change in factor B from -1 to 1 causes the equal change in response i.e. 6. Which indicates no interaction effect between two factors the parallel line in the charts indicates the absence of interaction. Figure 3.7 shows an example of a positive interaction where the factor B has more positive effect on factor A at high level than at low level. The unparallel line in the Figure 3.7 represents the positive interaction between these two factors. Figure 3.8 represents an example of negative interaction between A and B. The effect of factor B at level -1 of A is 28-25=3 and the effect of B at level 1 of A is 32-43= -11. The interaction effect between A and B is then (-11-3)/2= -7. The geometrical interpretation of negative interaction is also shown in Figure 3.8

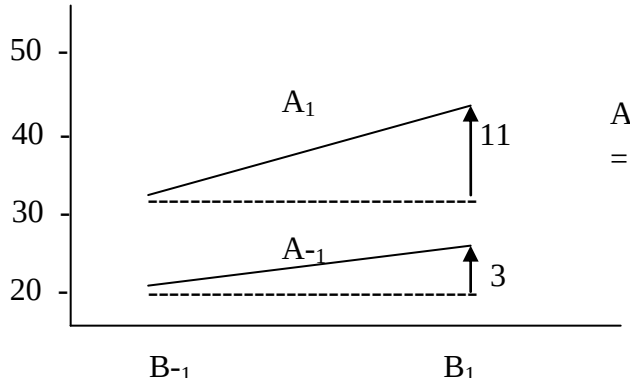
Factors		Average Response
A	B	
-1	-1	25
-1	1	31
1	-1	36
1	1	42



AB interaction $= \frac{6-6}{2} = 0$

Figure 3.6 No interaction effect

Factors		Average Response
A	B	
-1	-1	25
-1	1	28
1	-1	32
1	1	43



AB interaction $= \frac{11-3}{2} = 4$

Figure 3.7 Positive interaction effect

Factors		Average Response
A	B	
-1	-1	25
-1	1	28
1	-1	43
1	1	32

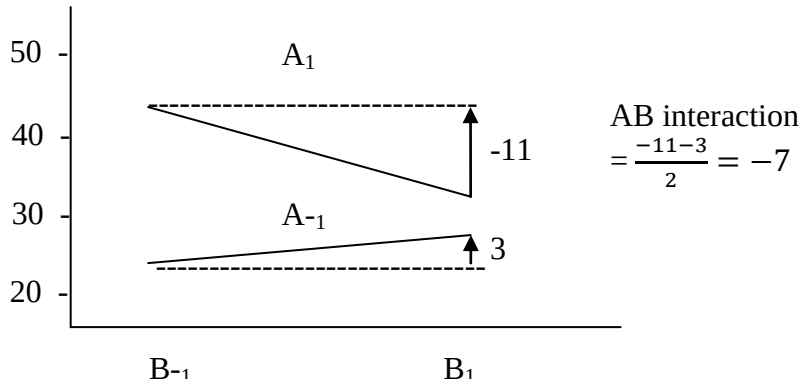


Figure 3.8 Negative interaction effect

Four factors in eight trails fractional factorial experimental design was used to investigate the effect of different factors on the strength of the fibres. It is a standard design to find the effect of factors by conducting lesser number of experiments. In the design, a three factor experiment in eight trails is implemented shown in Table 3.2 and the interaction ABD is relabelled as D. The levels of factors A, B and C remains the same as shown in Table 3.2 while the levels of ABC are treated as levels of factor D. This give the design matrix indicated in Table 3.3.

Standard order	Main Effects			Interaction Effects			
	A	B	C	AB	AC	BC	ABC
1	-1	-1	-1	1	1	1	-1
2	-1	-1	1	1	-1	-1	1
3	-1	1	-1	-1	1	-1	1
4	-1	1	1	-1	-1	1	-1
5	1	-1	-1	-1	-1	1	1
6	1	-1	1	-1	1	-1	-1
7	1	1	-1	1	-1	-1	-1
8	1	1	1	1	1	1	1

Table 3.2 Factor and interaction levels for a three-factor experiment in eight trials (-1 indicates low levels, 1 indicates high levels)

A	B	C	D
-1	-1	-1	-1
-1	-1	1	1
-1	1	-1	1
-1	1	1	-1
1	-1	-1	1
1	-1	1	-1
1	1	-1	-1
1	1	1	1

Table 3.3 Design matrix for four factors in eight trials

The trail values (-1or 1) for the interaction columns are then obtained by multiplying together corresponding column values the interaction terms involving A, B and C without D are given in Table 3.2. The interaction terms involving D are AD, BD, CD, ABD, ACD, BCD and ABCD. The columns for the two-factor interaction effects involving D are listed in the last three columns of Table 3.4.

A	B	C	D	CD	BD	AD
-1	-1	-1	-1	1	1	1
-1	-1	1	1	1	-1	-1
-1	1	-1	1	-1	1	-1
-1	1	1	-1	-1	-1	1
1	-1	-1	1	-1	-1	1
1	-1	1	-1	-1	1	-1
1	1	-1	-1	1	-1	-1
1	1	1	1	1	1	1

Table 3.4 Factor and interaction levels for experiment defined in Table 3.3

Comparison of columns in Table 3.2 and Table 3.4 reveals that not only ABC=D but also AB=CD i.e. the sequence of -1s and 1s in the AB column of Table 3.2 is identical to the sequence of CD column in Table 3.4. Similarly, AC=BD and BC=AD. The movement of letters around in the manner described above is based on the sound theory [106]. This allows to evaluate the effect of factors and interactions with lesser number of experiments. Table 3.5 shows an example of response table, the effect of factors and interactions are calculated by taking the average of response at two levels separately. The difference between these average responses of the same factor or interaction gives the total effect of the factor or interaction.

RO	SO	Y	A		B		C		AB		AC		BC		D	
			-1	1	-1	1	-1	1	-1	1	-1	1	-1	1	-1	1
6	1	73	73		73		73			73		73		73	73	
4	2	88	88		88			88		88	88		88			88
2	3	81	81			81	81		81			81	81			81
7	4	77	77			77		77	77		77			77	77	
3	5	83		83	83		83		83		83			83		83
1	6	81		81	81			81	81			81	81		81	
8	7	74		74		74	74			74	74		74		74	
5	8	90		90		90		90		90		90		90		90
Total		647	319	328	325	322	311	336	322	325	322	325	324	323	305	342
Number of values		8	4	4	4	4	4	4	4	4	4	4	4	4	4	4
Average		80.9	79.8	82.0	81.3	80.5	77.8	84.0	80.5	81.3	80.5	81.3	81.0	80.8	76.3	85.5
Effect			2.2		-0.8		6.2		0.8		0.8		-0.2		9.2	

Table 3.5 Response table example (RO = random order trial number, SO = Standard order trial number and Y = Response observed values)

A four factor two level fractional factorial deign was used in the present work. Statgraphics Plus 5.1 software was used to design and evaluate the experiments. The factors chosen were particle size, temperature, heating time, concentration. Particle size was selected due to the absence of its effect on the process in the literature. The temperature for the preparation of solution reported previously differs greatly depending on the solvent used, terpene was used as solvent in the research. Since, there was no data available on terpene. Hence, it was necessary to investigate the effect of the temperature. Heating times reported for the different solvents were completely different e.g. paraffin solutions were reported to be heated for 48 hour while decalin solutions

were heated till the dissolution occurs. Hence, it was necessary to investigate the optimum time for terpene based solution. Concentration was chosen as factor due to complete absence of the data on the terpene based gel spinning process. Different percentages were reported in the literature for different solvents. Initial experiments were conducted to find the levels for each factor.

3.8 Optical Microscope

An optical microscope is an instrument for viewing objects that are too small to be seen by the naked eye. In this work, optical microscopy was used to magnify the blended polymer samples to investigate the blending. The optical microscope magnifies an image by sending a beam of light through the object as shown in the systematic diagram of Figure 3.9. The condenser lens focuses the light on to the sample and the objective lenses magnify the beam, which contains the image, to the projector lens or the digital camera.

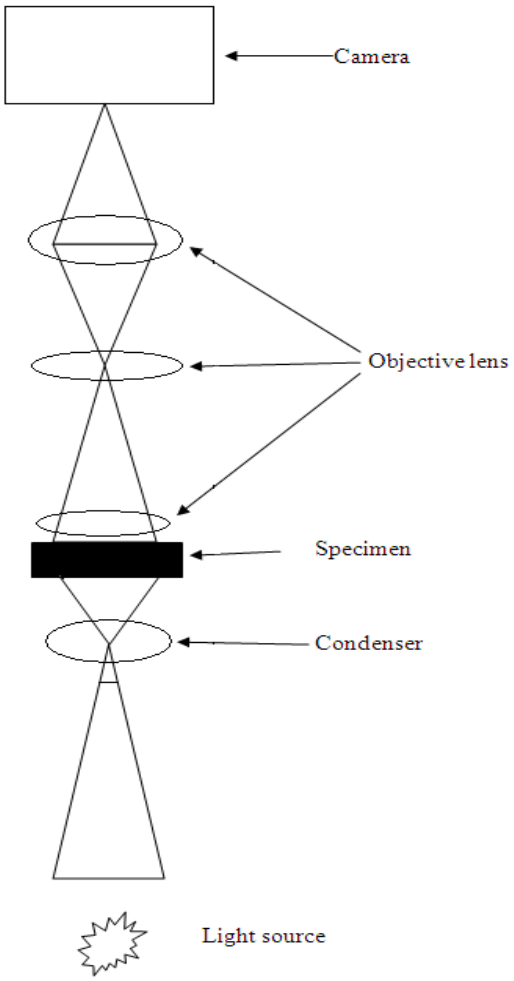


Figure 3.9 Systematic diagram of optical microscope [95]

3.9 Scanning Electron Microscopy

Scanning electron microscope (SEM) is a very useful instrument to magnify the very small specimens which cannot be seen by a normal optical microscope. SEM uses a beam of electrons which is generated at the top of the microscope. The part that produces this beam is called the electron gun. The electron beam follows a vertical path through the column of the microscope then passes through the condenser lens that focuses the beam down towards the sample. A scan generator scans the beam of electrons in a raster pattern across the sample surface. When these electrons strike the sample, they cause the ejection of the secondary electrons that are collected by one of the detectors building up an image of the sample on the monitor. Figure 3.10 shows a schematic diagram of SEM.

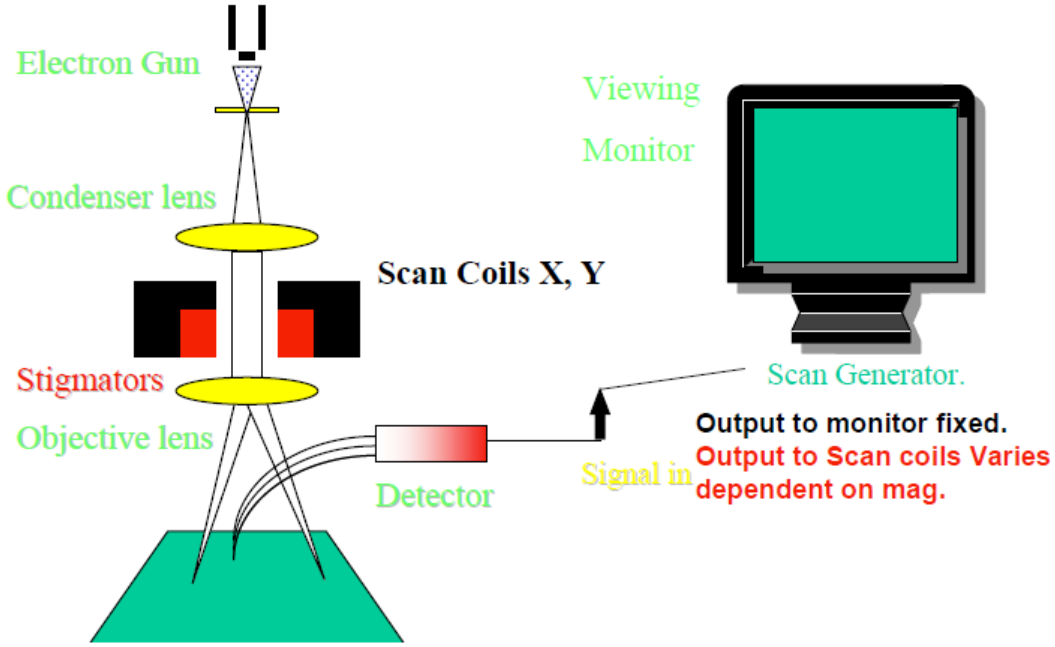


Figure 3.10 Schematic diagram of an SEM [107]

Since SEM relies on electrons to generate images, the samples need to be electrically conductive. Materials such as metals, which are very conductive, do not require any preparation to be observed under SEM. However, materials such as polymers and ceramics are poor conductors so cannot be observed directly under SEM. To overcome this limitation these non-conductive materials are coated with a fine layer of a conductive material. This is achieved by using a sputter coater shown in Figure

3.11. The sputter coater coats the samples with thin (nm) layer of gold. Sputtering is done under vacuum in the presence of argon gas. RF power (in the case of RF generated plasma) is applied on the sputter target i.e. gold (which generates a plasma) and argon atoms get excited and start bombarding the target which results in etching of the gold. These etched gold atoms are deposited on the surface of the sample providing a thin conductive coating.

Figure 3.11 Image of Polaron SC7620 Sputter coater

In this work, a Hitachi S-4300 FE SEM shown in Figure 3.12 was used to observe the morphology of the fibres and the coated films. The specimens were coated with gold for 45-60 sec using a Polaron SC7620 Sputter coater.

Figure 3.12 Image of the Hitachi S-4300 FE SEM [107]

3.10 Tensile Testing

Tensile test is widely used to determine the wide variety of mechanical properties of fibres. In a typical tensile test, a sample is extended at a constant rate and the load needed to maintain this rate of extension is measured by a load cell, which is connected to a computer. The computer then records the data and generates load vs. elongation graph. A typical stress strain curve is shown in Figure 3.13. This graph can be used to calculate true stress (ε), strain (σ), Young's modulus (E) and other mechanical properties.

Stress (ε): The force (F) on the object divided by the cross-sectional area (A), expressed in Nm^2or Pa. Equation 3.2 express the stress in mathematical form.

$$\varepsilon = \frac{F}{A} \qquad (3.2)$$

Strain (σ): The ratio of elongation with respect to the original length of the fibre. Mathematical expression of strain is shown in Equation 3.3.

$$\sigma = \frac{l' - l}{l} \tag{3.3}$$

Where *l* is the original length of the material an *l'* is the final length

Young's Modulus (E): A measure of a material's stiffness, the higher the Young's modulus the stiffer the material. It is the ratio of stress to strain on the loading plane along the loading direction. Equation 3.4 expresses the Young's modulus in mathematical form.

$$E = \frac{\varepsilon}{\sigma} \tag{3.4}$$

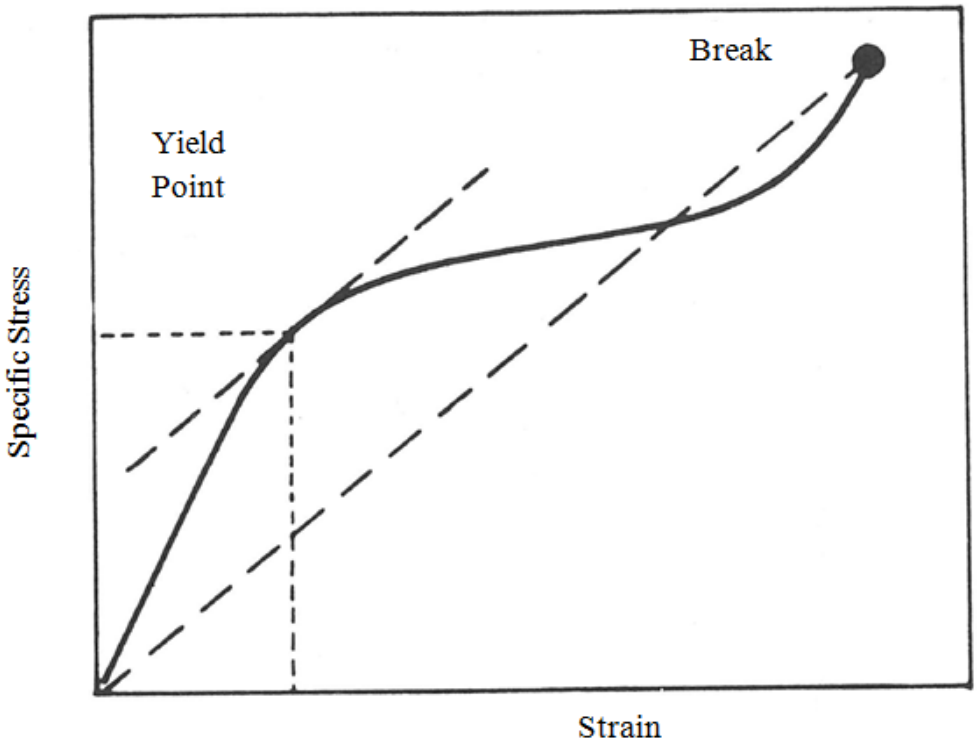


Figure 3.13 Stress-strain curve of fibre [108]

In this project, tensile testing was conducted using the Instron 3345 (Figure 3.14). The ASTM standard D 3822 was followed for fibre testing. The Instron 3345 was connected to a computer installed with Bluehill material testing software to record data and generate graphs. Fabrics coated with UHMWPE were tested using the same instrument and implementing British standard BS EN ISO 1421 and BS 4303.

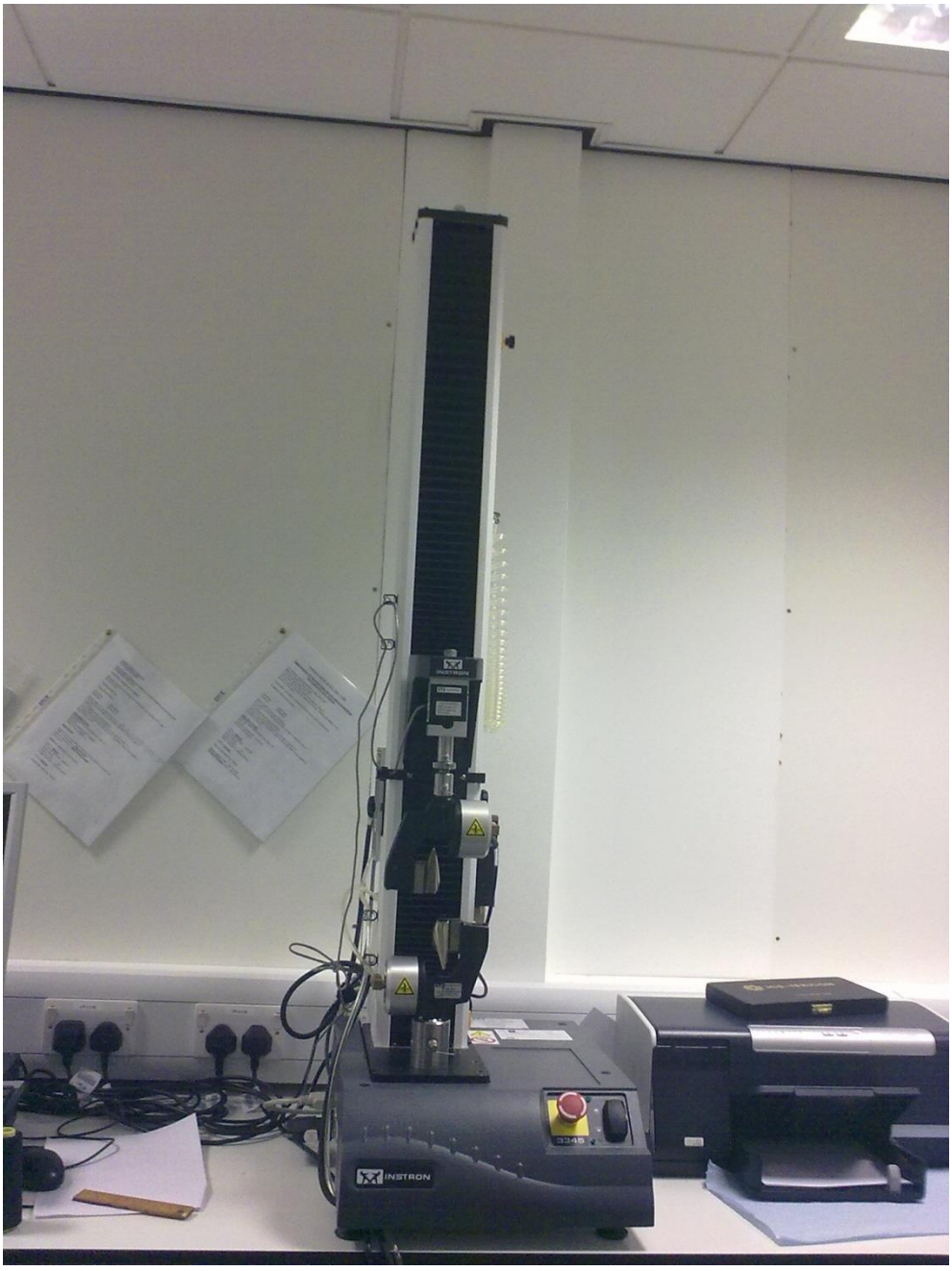


Figure 3.14 Image of Instron 3345 tensile tester

3.11 Fabric Coating

The preliminary coating experiments were carried out by utilising the dip coating. Which paved the way for the more controlled coating process the wire rod

coating method was also used. While a custom made method was also used to understand the interaction of coating solution and the fabric. Which lead to the designing of a mechanised coating process.

In this project, the Coatema Basecoater BC 06 was used to coat the fabrics with UHMWPE. The machine uses the knife over roller principle to coat the fabric. The different parts and their operations in the machine are described in Figure 3.15 and Figure 3.16.

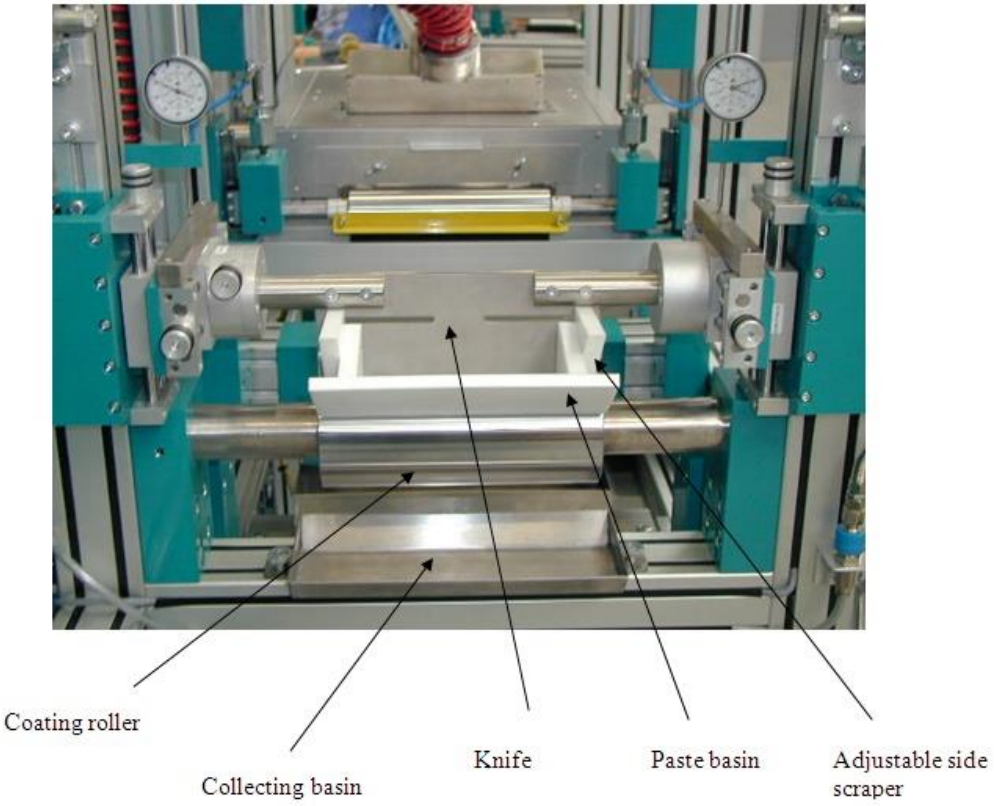


Figure 3.15 Coatema Basecoater BC 06 coating machine

Figure 3.16 Coatema Basecoater BC 06 rear view

The Coatema Basecoater BC 06 machine was modified to coat the UHMWPE on to the fabrics. Two heaters were installed onto the knife to heat the UHMWPE solution as shown in Figure 3.17.

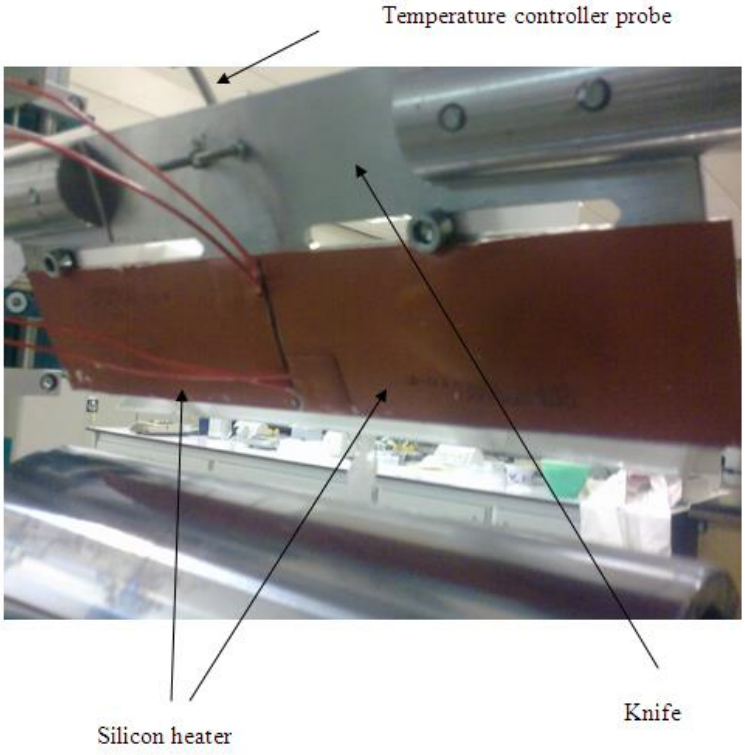


Figure 3.17 Heater installed on modified knife with temperature controller probe

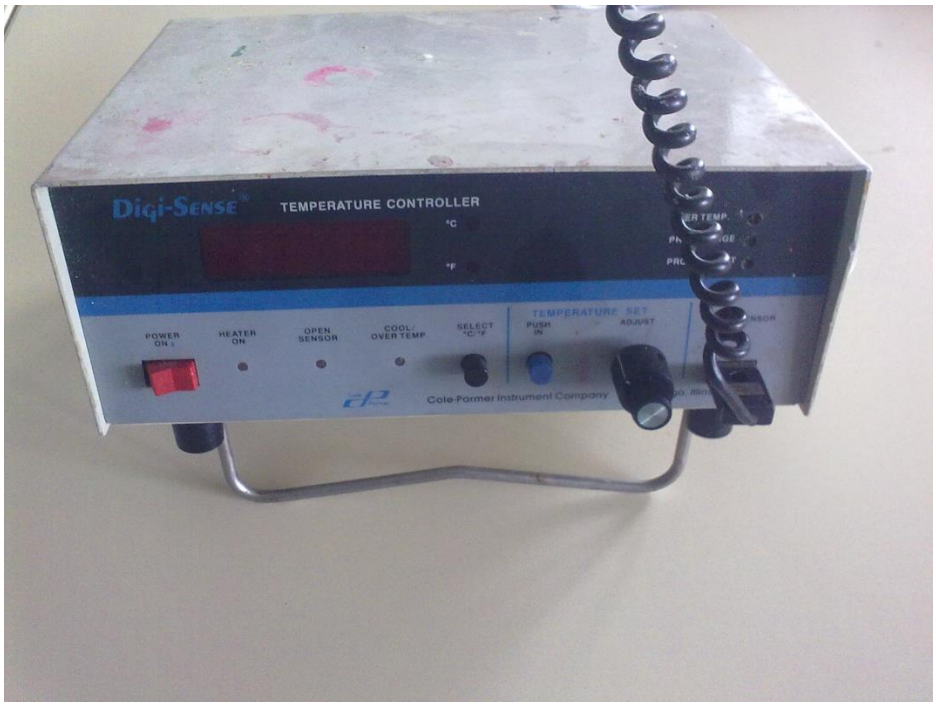


Figure 3.18 Temperature controller

Since the heater needs to be controlled to maintain the temperature at the certain point. A pulsating temperature controller shown in Figure 3.18 was used to control the temperature. The temperature controller was installed onto the knife to control the temperature of knife within an acceptable range. The modifications made in the machine will be discussed in detail in Chapter 5.

3.12 Summary

This chapter presented the methodology which was planned to achieve the objectives described in section 1.4. The materials used in this research were also presented. The chapter also described the working principle of the methods used in this research.

After the methodology had been formulated the next chapter contains the experimental work carried out to achieve the first five objectives.

Chapter 4 **Investigation of Fibre Manufacturing Process of UHMWPE**

4.1 Introduction

A two pronged approach was adopted to develop an environmentally friendly process for the production of UHMWPE fibres. In the first approach, the blends were prepared to find a solvent free process, while the second approach investigated the natural solvents for the preparation of UHMWPE fibres from gel spinning. An experimental design was also implemented to find the factors, which affects the strength of the fibres. One of the problems associated with the UHMWPE fibres are the high number of entanglements, which results in weaker fibres. Ultrasound treatment was investigated to find its effect on the entanglements of the polymer chains in UHMWPE fibres.

4.2 Extrusion of Blends

The extrusion of blends reported previously had shown improvement in the mechanical properties of the fibres. While in the previous research the blends were prepared by gelation/crystallization from solution which also utilises the same kind of petrochemical solvents as gel spinning in the present work the blends prepared by melt extrusion has been investigated. To extrude the polymer the understanding of the thermal behaviour i.e. at what temperature polymer starts melting, temperature at which the polymer is completely melted and the temperature of polymer decomposition is very important. To understand the thermal behaviour of the polymer DSC (differential scanning calorimetry) was used. The DSC charts of both grades of polymer are shown in Figure 4.1 and Figure 4.2. The melting points indicated by the DSC graphs are 130-145^{o}C and 125-145^{o}C for GUR 2122 and GUR 4120 respectively. The melting temperatures indicated by the DSC graph are slightly higher than the melting point proposed by the supplier i.e. 130-135^{o}C. (Refer to Figure 3.2 for explanation of the DSC graph)

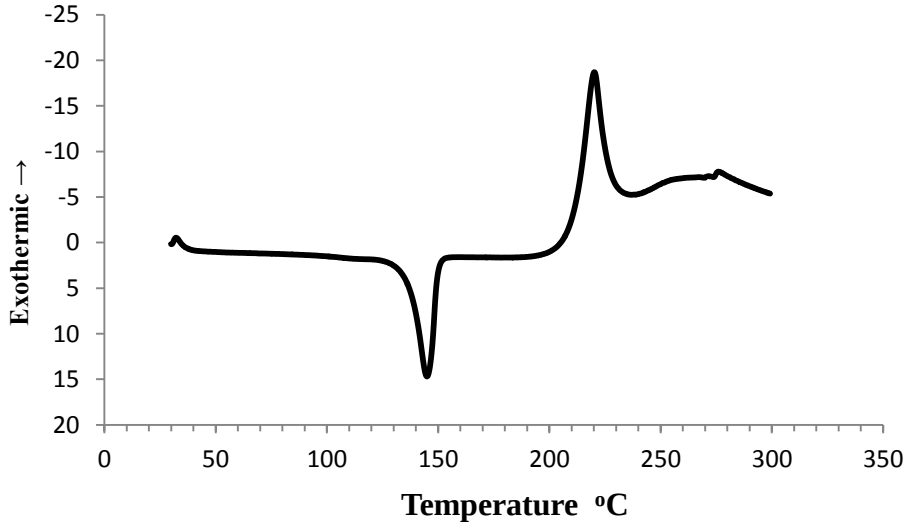


Figure 4.1 DSC graph of GUR 2122 polymer

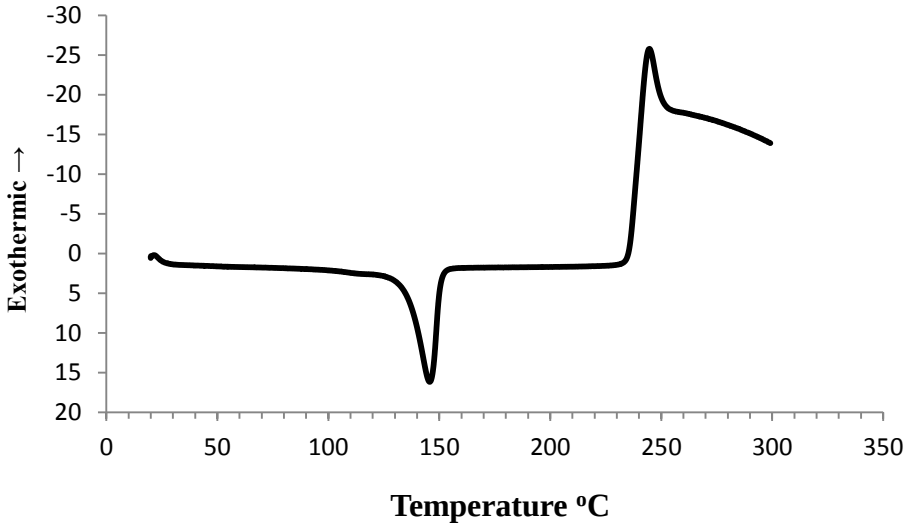


Figure 4.2 DSC graph of GUR 4120 polymer

Blends of UHMWPE with other polymers by gelation/crystallization were reported to improve the strength of the fibres. There were no data available regarding the blends of UHMWPE with other polymers by melt spinning. It was decided to investigate blends of UHMWPE with polypropylene due to similar processing temperature. Two blends were prepared; one with 95% PP and 5% UHMWPE and second with 99% PP and 1% UHMWPE. The blends were homogenously mixed by stirring. To achieve better blending, the screw extruder with a mixing head was chosen to extrude the blends. Extrusion was conducted at following temperature settings

1st Zone at 190°C

2nd Zone at 220°C

3rd Zone at 220°C

Metering Pump at 230°C

The blends were fed into the extruder and the extrudate passed through an air gap of 75 mm followed by quenching in water at room temperature. The filaments were then wound onto a bobbin.

It was observed that the continuous extrusion was difficult due to frequent breakage of the filament which was uneven with thin and thick places. These thin places were causing the breakage. This was thought to be due to the presence of UHMWPE powder particles which were not blending with the PP on molecular level. To check this hypothesis DSC of the samples was conducted.

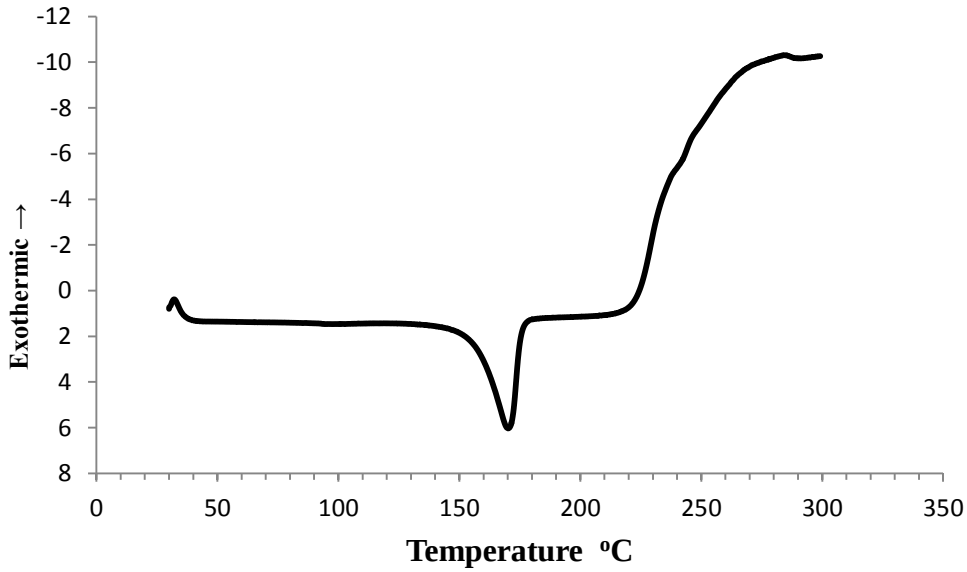


Figure 4.3 DSC graph of Polypropylene

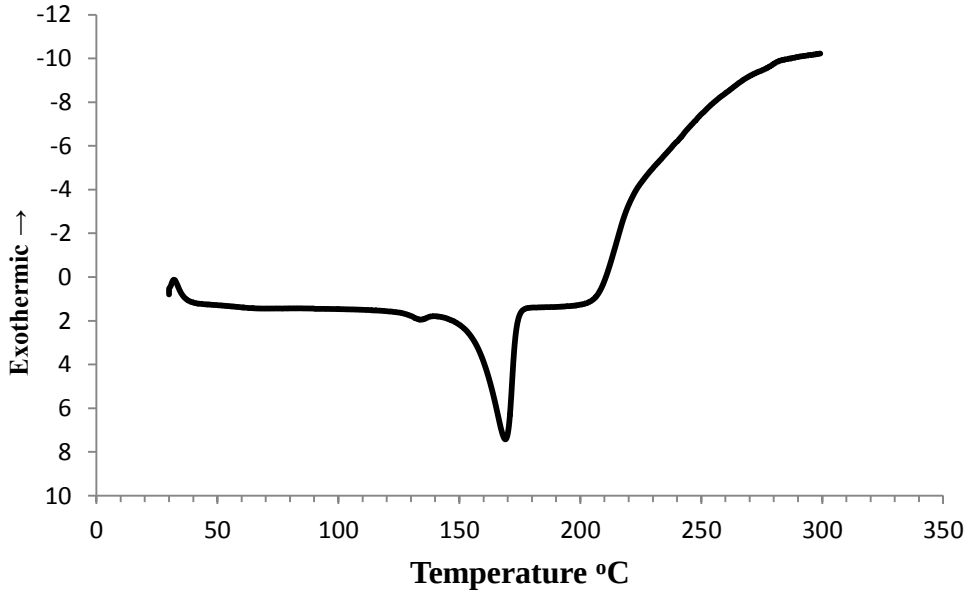


Figure 4.4 DSC graph of Polypropylene and UHMWPE blend

The DSC of polypropylene and UHMWPE were done separately to determine their thermal behaviour. Figure 4.3 and Figure 4.2 show the DSC graph of PP and UHMWPE respectively. Once the thermal behaviour of both PP and UHMWPE had been investigated separately, the DSC of the PP and UHMWPE blend was conducted to investigate whether PP and UHMWPE are blending or not. The DSC graph of PP/UHMWPE blend shown in Figure 4.4 has two peaks, one at 135^{o}C and one at 167^{o}C. It is clear from the DSC chart that the first peak at 135^{o}C was due to the presence of UHMWPE while the second peak at 167^{o}C was due to polypropylene. As both polymers showed two separate peaks, this points to the lack of blending between the two. To prove this hypothesis microscopic pictures were also taken.

As shown in Figure 4.5 the thin places were resulted from the unmixed UHMWPE particles. Since the UHMWPE contains very long polymer chains which causes the polymer chains entanglement resulting in very low MFI. Due to this low MFI the UHMWPE particles sustained their particle form causing thin places in the fibre. To verify this negative effect of UHMWPE on the strength due to lack of blending, microscopic images of blend film were also taken as shown in Figure 4.6. In the microscopic image of the blend film, the particles of UHMWPE are visible indicating the lack of or perhaps complete absence of blending between the two polymers.

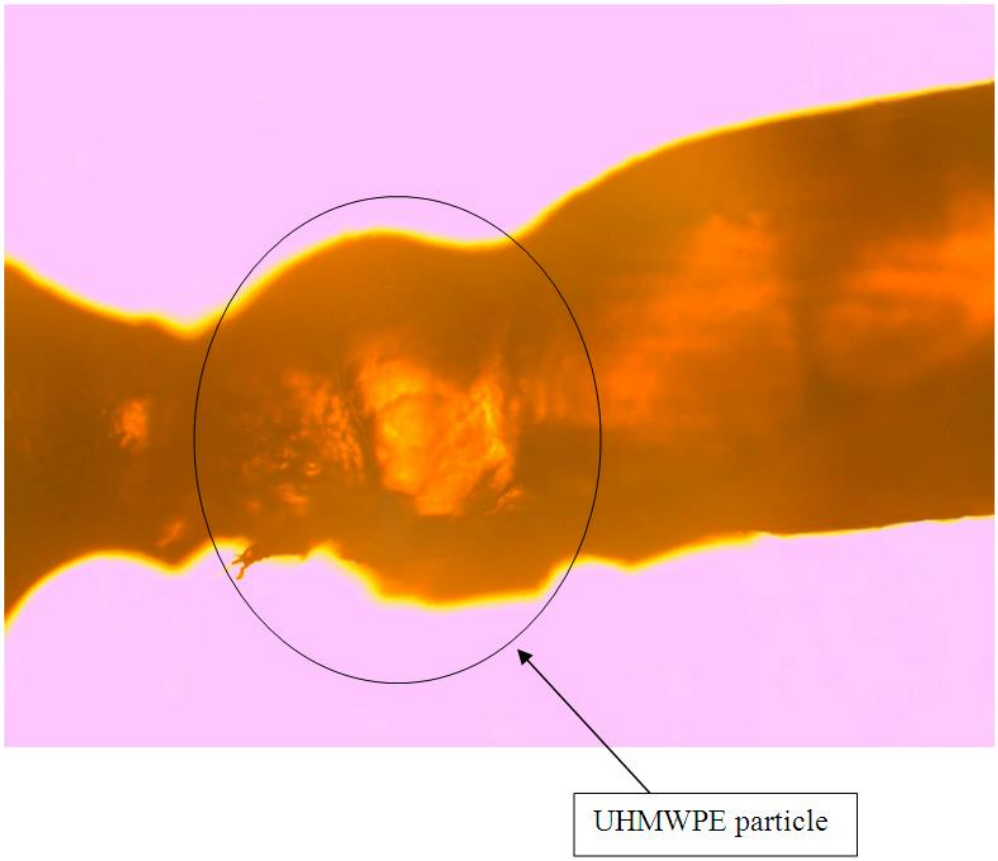


Figure 4.5 Microscopic image of PP/UHMWPE blend filament

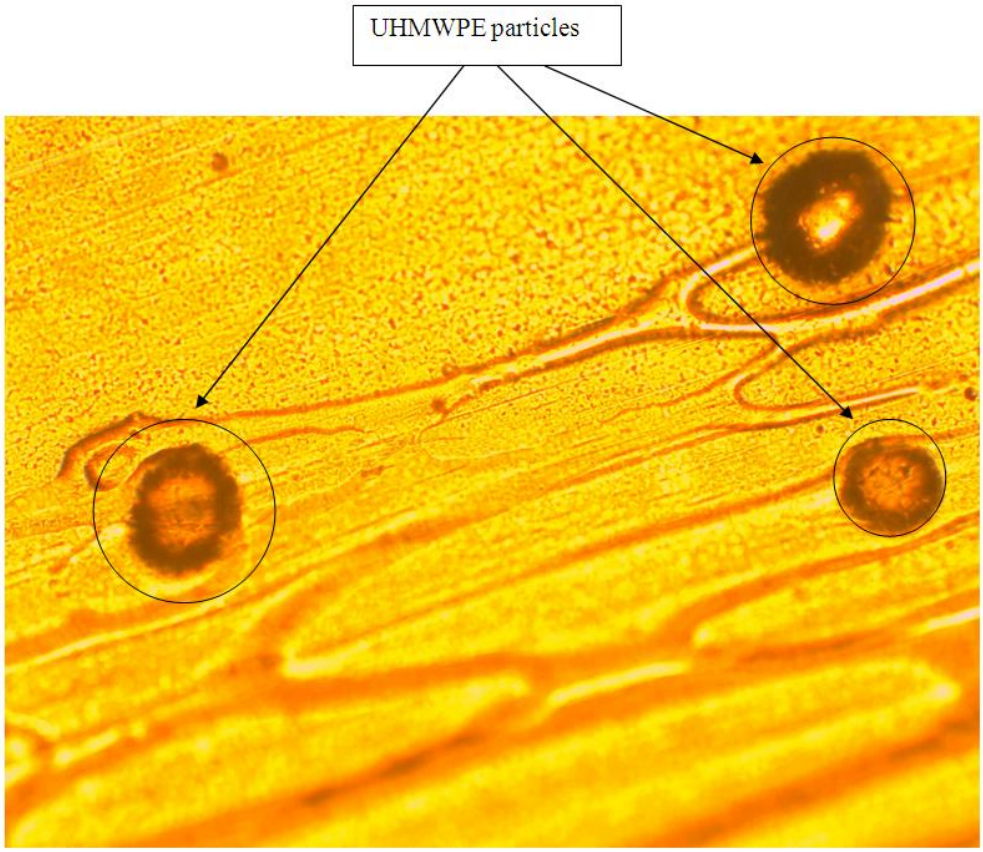


Figure 4.6 Microscopic image of PP/UHMWPE blend film

The extrusion of blends with a different percentage i.e. 1% and with a different polymer (polyethylene) gave the same results. This lack of mixing was due to the very high molecular weight of the UHMWPE which results in high viscosity not allowing UHMWPE to mix with other polymers.

The lack of polymer mixing in blended fibres lead to the abandonment of the melt spinning experiments. The research was then focused on the second approach which was to find an alternative natural solvent to the petrochemicals.

4.3 Experiments with Natural Oils

All the chemicals known for the gel spinning of UHMWPE were organic solvents. The chemistry of the oils has been described in section 2.8 which shows the high number of hydrocarbons present in these natural oils. Therefore, the most appropriate alternatives could be the oils from natural sources. It was decided to experiment with natural oils, the availability and cost of the oils being prime factors to select or eliminate certain oils. Sunflower oil, palm oil and orange terpene were selected to conduct further experiments in order to find a natural alternative of petrochemical solvents.

4.3.1 Sunflower Oil

A 5% (w/v) solution of UHMWPE in sunflower oil was prepared. The solution was heated to 110^{o}C with slow stirring. The changes in the solution were closely monitored to check the emergence of the Weissenberg effect i.e. the rise of the polymer on to the stirrer. The heating of the solution formed a clot of the polymer in the solution rather than a homogenous polymer solution. A separate solution with the same concentration was heated to 120^{o}C and again no Weissenberg effect emerged rather a clot was formed. The same experiment was repeated with the increase of 10^{o}C until 200^{o}C but no dissolution was observed each experiment resulted in the formation of polymer clot. The presence of complex chemicals like phospholipids, sterols and waxes can be the reason of this complex behaviour. Further experiments with sunflower oil were abandoned.

4.3.2 Palm Oil

A 5% (w/v) solution of UHMWPE in palm oil was prepared and heated to 120^{o}C and with slow stirring to form the polymer solution. The solution was heated for

30 min. The solution was closely monitored for the emergence of the Weissenberg effect. The heating of the solution did not resulted in a homogenous polymer solution. The polymer rather formed a clot leaving the oil. Separate solutions were prepared with the same concentration and heated from 120^{o}C to 200^{o}C with the increase of 10^{o}C. All the experiments resulted in polymer clots. The reason of this was the presence of similar kind of complex chemicals e.g. tocotrienols, sterols, phosphatides, and sterols, in palm oil as in sunflower oil.

4.3.3 Terpene Oil

A solution was prepared with 5% (w/v) of UHMWPE in terpene. The solution was heated to 110^{o}C with slow stirring. It was observed for the Weissenberg effect, on the emergence of Weissenberg effect stirring was stopped and the solution was kept heating at 110^{o}C for 30 min. It was observed that the solution formed a homogeneous gel. Since the orange terpene does not contains other impurities in contrast to above mentioned oils the impurities did not affected the dissolution process. To determine the maximum temperature at which the gel can be prepared, separate solutions with 5% (w/v) concentration were prepared and heated to different temperatures from 120^{o}C to 170^{o}C at 10^{o}C intervals. The experiment was not conducted above 170^{o}C due to the lower boiling point of the terpene i.e. 176^{o}C.

The success in producing the gel led to the second step of extrusion in the gel spinning process. To keep the extrusion process simple and to find the processability of the terpene gel, the ram extruder was chosen due to simpler mechanisms. The gel was cut in small pieces (approximately 5 mm$^{3)}$ and fed into the barrel of ram extruder. The barrel was heated to 150^{o}C. The gel was left for 10 min in pre-heated barrel to melt the gel evenly before extruding. The extrudate was quenched by passing it through a 10 cm air gap. The extrudate was then passed through a water bath at ambient temperature at a speed of 2 m/min. After quenching, the filaments were wound onto the bobbin. The filament prepared by the terpene gel showed an interesting phenomenon. There was not much excess oil left in the filament collected on the bobbin. Due to the safe nature of the terpene oil the traces of the terpene were removed by leaving fibres for 48 hr under ambient conditions.

The experiments with the natural oils proved that the terpene could be the potential alternative to petrochemical solvents.

4.3.3.1 Additives

The experiments with terpene showed some of the solutions turned into a dark colour due to the oxidation of the polymer, while some remained normal. It was overcome by adding 2,4-Dimethyl-6-tert-buthylphenol antioxidant in the spinning solution. The experiments showed addition of 1% (w/v) 2,4-Dimethyl-6-tert-buthylphenol in the solutions was enough to overcome this problem.

The extrusion of the terpene gel on the ram extruder presented many problems; one of them was the stickiness of the gel around and on the die exit. The gel was sticking to the die exit and around it as it emerged from the die exit hole. This stickiness of the gel was causing unevenness of the filament and the frequent breakage. Aluminium stearate was added into the gel to reduce this problem by previous researchers [10]. However, no data was available on the terpene based gel spinning process. To investigate the effect of aluminium stearate on terpene based gel extrusion different percentages of aluminium sterate 1%, 2%, 3% and 4% were added. The addition of 1% aluminium stearate improved the extrusion process. However the addition of more than 1% did not improve the process any further. At a high percentage of aluminum stearate, small clots started to appear in the filament creating weak spaces.

4.4 Solvent Removal

The removal of the solvent from the filaments after extrusion is vital in gel spinning. As discussed in chapter two different researchers used different methods (chemical or physical) to remove solvents depending on the solvents used to extrude the fibres. Solvent removal is one of the most important factors when considering the economy of the process. The sole reason for this process is to get rid of the solvent, as this step has no effect on the physical properties of the fibres.

It was important to find the most economical process to remove terpene from the fibres. The absence of data presented a new challenge. As one of the objectives of the project was to develop an environmentally friendly process, no harmful chemical could be utilised. One disadvantage of using a chemical to remove solvent was the increase in the cost of the process. It was decided to investigate the removal of the solvent by physical methods.

To investigate solvent removal, the extrudate was passed through the water bath. In the water, the fibres are quenched and due to the lower temperature of water bath the

temperature of the fibres dropped which caused phase separation. The phase separation is a common characteristic of the gel. For a polymer to dissolve into a solvent or remain as a homogeneous solution, it must satisfy the following equation: [9]

$$\Delta F_m = \Delta H_m - T\Delta S_m \quad (4.1)$$

where, ΔF_m = Free energy of dissolution

T = Absolute temperature

ΔH_m = Heat of dissolution

ΔS_m = Entropy of dissolution

For a non-polar polymer dissolving into a non-polar solvent, the situation where $\Delta H_m \geq 0$ and $\Delta S_m \geq$,can only occur when T is high enough to facilitate $\Delta H_m < T\Delta S_m$. A homogenous solution of a non-polar polymer into a non-polar solvent prepared at a high temperature gets unstable when the temperature decreases and the balance of the system is upset and the polymer coagulates from solution.

UHMWPE is non-polar polymer with high molecular weight. It dissolves at above 130^{o}C. As discussed previously at this temperature the process of dissolution meets $\Delta H_m < T\Delta S_m$ during the spinning process when the extrudate entered the water bath at ambient temperature which was much lower than the temperature of phase separation. The phase separation occurred and solvent left the solidified fibres to enter the water. The phase separation continued when the filaments were kept at room temperature. It was found that the solvent could be removed from the filaments by passing through the water and leaving at room temperature. To investigate whether the solvent is completely removed from the fibres DSC thermographs of the powder, gel and dried fibres were taken which are shown in Figure 4.7, Figure 4.8 and Figure 4.9 respectively.

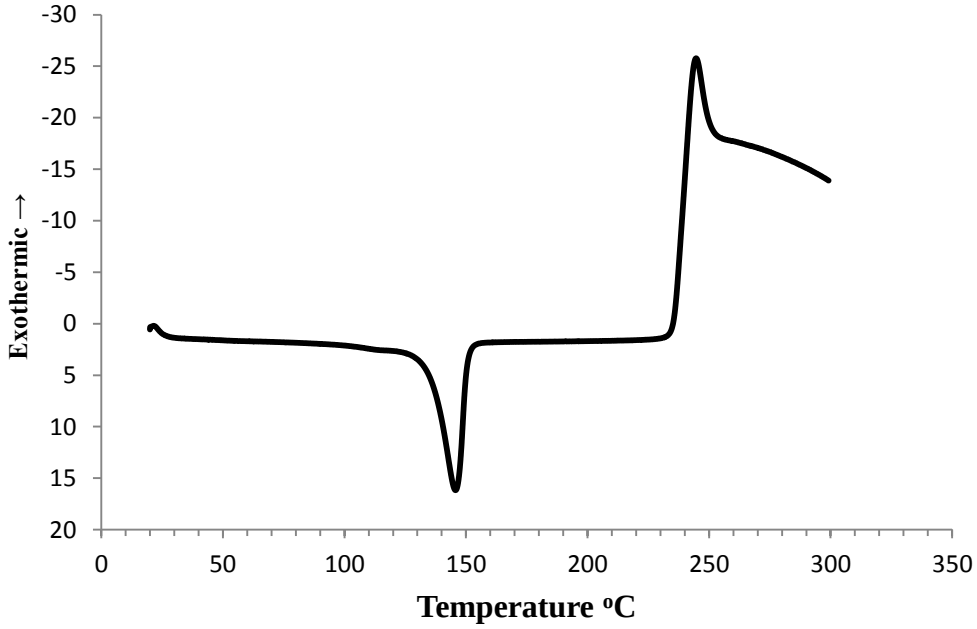


Figure 4.7 DSC thermograph of UHMWPE powder

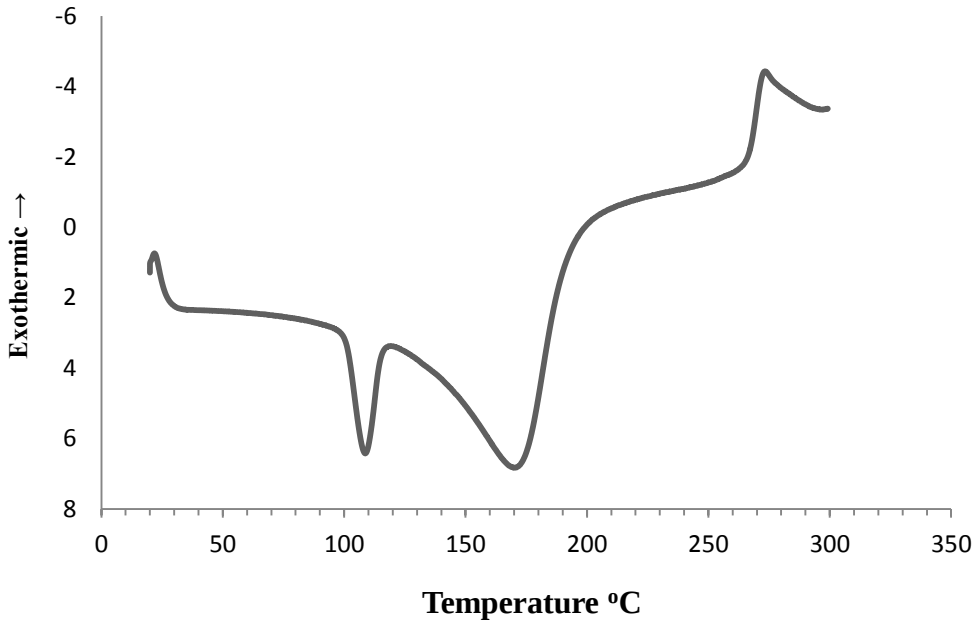


Figure 4.8 DSC thermograph of Gel

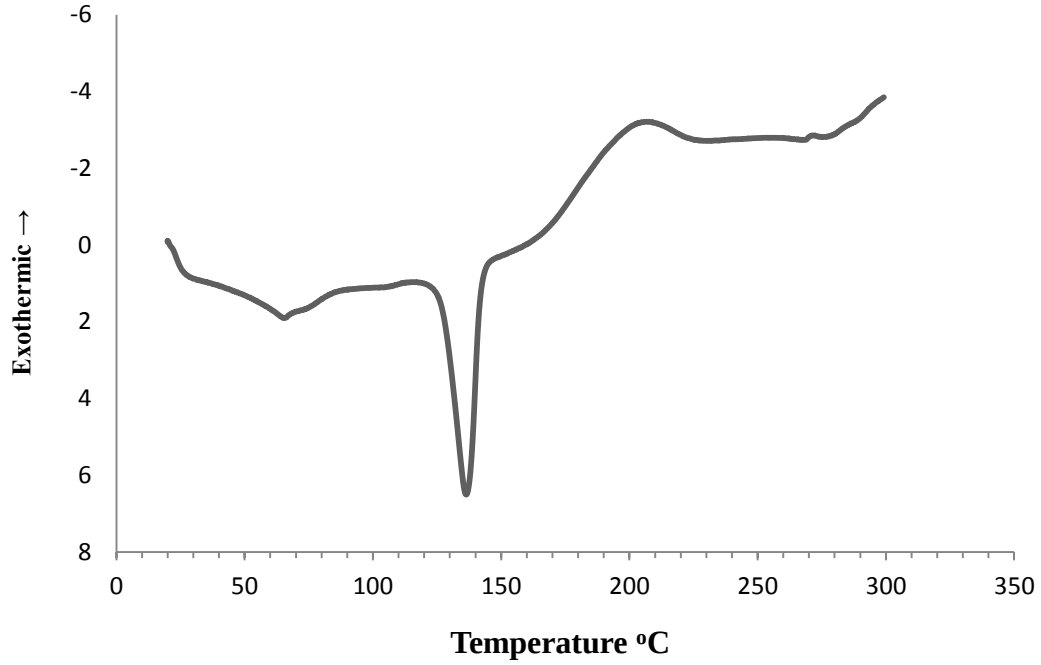


Figure 4.9 DSC thermograph of UHMWPE fibre

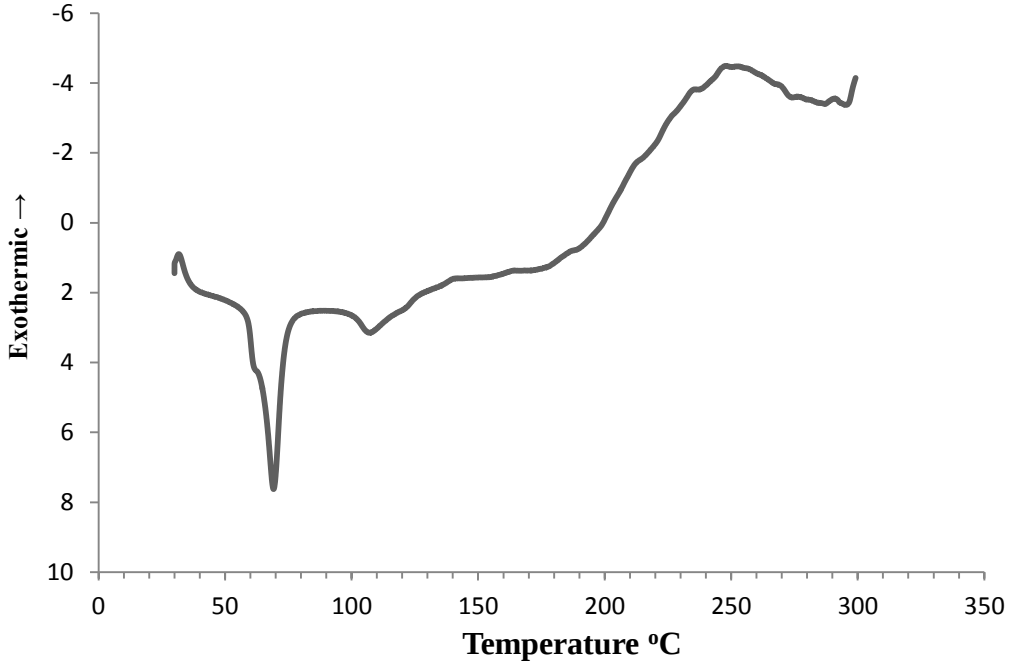


Figure 4.10 DSC thermograph of aluminium stearate

In the DSC thermograph of the UHMWPE powder in Figure 4.7, the peak appears around 137^{o}C corresponding to melting of the polymer. Figure 4.8 shows the DSC thermograph of gel prepared with terpene. The first peak appears around 110^{o}C indicating the melting point of the polymer which is lower than that indicated in Figure

4.7 due to the imperfection in the crystal of polymers caused by the gel formation and presence of the terpene. The second peak appears at 170^{o}C indicating the boiling point of the terpene. The two different peaks in Figure 4.8 indicate the presence of polymer and solvent. The DSC thermograph of UHMWPE fibre shown in Figure 4.9 shows one large peak around 138^{o}C indicating the melting point of the UHMWPE, which was increased from 110^{o}C in the gel form to 138^{o}C in the fibre form; the absence of second peak in the fibre, shows the complete removal of the terpene from the fibres. A small peak around 70^{o}C is due to the presence of aluminium stearate as shown in the Figure 4.10.

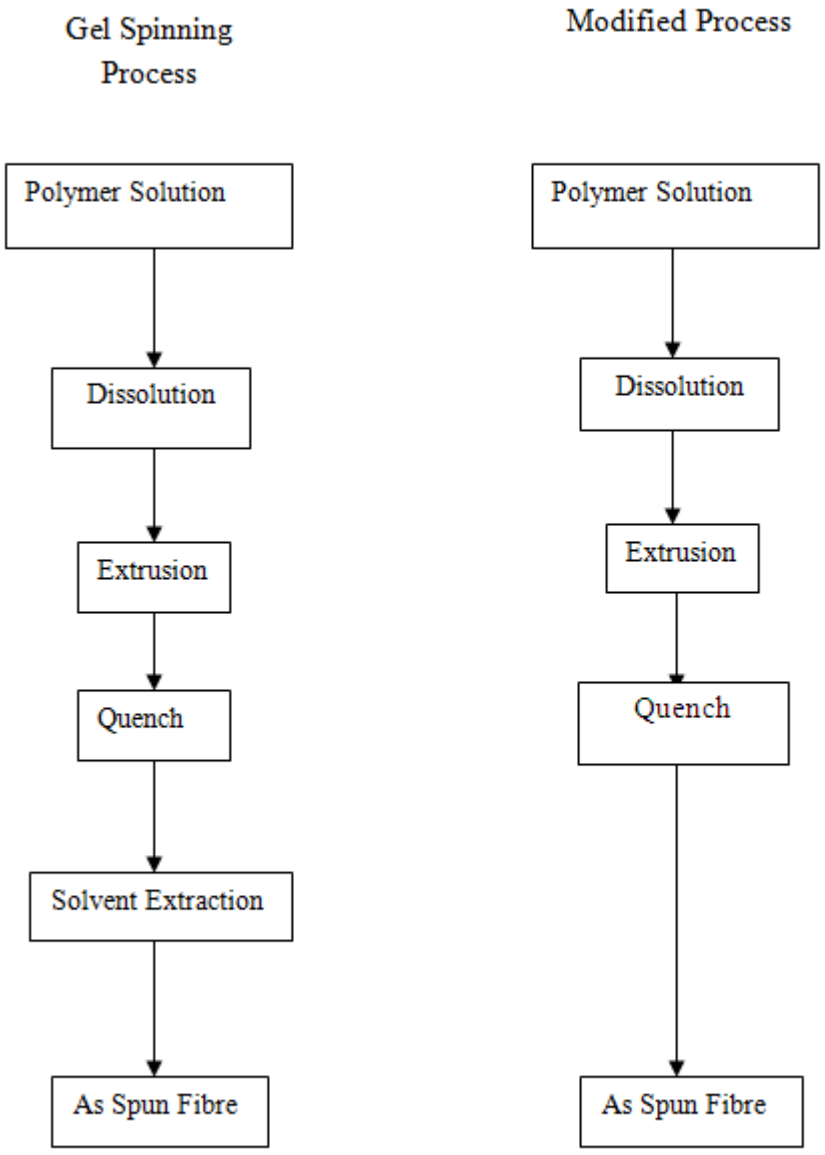


Figure 4.11 Comparison between conventional gel spinning process and modified gel spinning process

A comparison between conventional gel spinning process and terpene based modified gel spinning process is shown in Figure 4.11. Both processes involve the preparation of solution. In the second stage of both processes, the solution is heated to dissolve the polymer. Polymer solution is then extruded and quenched to form gel like fibre here the modified process deviate from the standard one. The water quenching stage in modified process also performs the task of solvent extraction. While in the case of conventional gel spinning process a separate solvent extraction process is performed

by using evaporative solvents e.g. n-hexane, hexane, cyclohexanone, xylene, gasoline, toluene etc. which adds to the cost of the process. Hence, the elimination of the solvent extraction process not only eliminates the use of hazardous chemicals it also reduces the cost of the process. Since the extraction is performed as a separate process which involves the running cost while in the case of modified process the extraction takes place simultaneously at the quenching process eliminating the need for a separate process.

The successful preparation of the gel fibres from the terpene completed the first objective of the research described in section 1.4 which was to indentify a sustainable, environmentally friendly and user friendly solvent. Since terpene is derived from orange peel it is sustainable, it is also biodegradable and safer to use as described in section 2.8.3. The process developed also does not need any secondary solvent for the removal of the spinning solvents which was the second objective of this research. The elimination of the secondary solvent meant elimination of the cost associated with it and the elimination of the health and environmental hazards. The third objective of the research was to eliminate the solvent extraction stage. The process described in Figure 4.11 does not contain a separate solvent elimination stage rather the solvent is removed by passing the gel fibres through water bath and by evaporating traces of the solvent at ambient condition.

The completion of the first three objectives set in the section 1.4 which were the identification of a sustainable, environmentally friendly and user friendly solvent for the production of UHMWPE, identification of a process which eliminates the use of extraction solvents and development of a process which eliminates the solvent extraction stage lead to investigate the effect of different factors through systematic experimental approach on the strength of the fibres which was the fourth objective of the research.

4.5 Experimental Design

The fourth objective of the research was to investigate the effect of different factors through systematic experimental approach on the strength of the fibres. Due to the many factors, which can affect the process, experimental design was implemented in order to find out the factors that affect the process. Four factors were identified i.e. polymer particle size, temperature, heating time and concentration. The first three

factors were chosen because there was no data available in present literature on the effect of these factors. Concentration was chosen due to contradiction in the available literature. One point of view which was presented by Lemstra and his co-workers [61] was that the lower concentration results in higher strength while Prevorsek [4, 49] said with the increase in concentration strength of the fibres increases. There was a need to establish which opinion was correct for the terpene based modified process.

A two level fraction factorial experimental design having four variables (polymer particle size, temperature, heating time, concentration) was used to evaluate the effect of these variables on the fibres strength. Two levels were chosen to avoid unnecessary complication in the experimental design and to keep the number of experimental runs to a minimum. The experimental design is explained in detail in section 3.7. The extruded fibres were evaluated on the Instron tensile tester to evaluate the tensile strength of the fibres, which was used as a response in the experimental design.

The first stage in the application of the experimental design was to find the two levels at which the experiment would be conducted. The problem with the new process was the absence of any data in the literature. The SEM images of UHMWPE polymer were taken to find the size of the particles since it was found that the particle sizes differ greatly. The particles with sizes greater than 150 micron and less than 250 micron were set as level one and particles with sizes greater than 250 micron were set as level two. The different sizes were separated by sieving. The temperature levels were relatively easy to set. The gelation of the polymer solution in terpene occurs around 120^{o}C so the level one was set at 130^{o}C. Level two was a more complicated as according to the information available there was a wide range of temperatures at which the solutions were prepared with different solvents. The maximum at which the solution could be made was 176^{o}C which is the boiling point of terpene. Level two was set at 150^{o}C to avoid boiling of the terpene during the gel preparation process. Setting the level for the heating was also difficult due to the complete absence of any data regarding terpene for the gel formation. The available data had significant differences from decalin, which has just 40 min heating time at most to paraffin which needs to be heated for 48 hr. It was decided to keep the level at a moderate level. From the initial experiments, it was found that the gel could be made by heating the solution for 40 min after reaching the temperature. It was decided to set the level one for heating time at 1 hr and level two at 3 hr. Deciding the levels for the concentration was more challenging than deciding the

levels for other factors. Experiments conducted by researchers with decalin showed that the fibres can be prepared with the concentrations as low as 0.5% but with the same percentage of polymer in paraffin no yarn could be extruded. This meant that an initial experiment had to be conducted to find the lowest possible concentration at which fibres could be produced with terpene. Gels were prepared with 0.5%, 1%, 2% and 3% and all the gels were extruded on the ram extruder at 150^{o}C. The fibres were collected on the bobbins. It was found that only 2% and 3% gel had sufficient viscosity to be extruded; other gels with lower concentrations did not have the sufficient viscosity to be extruded into the yarn. The fibres extruded from the 2% and 3% gel were collected on the bobbin and left to dry in ambient conditions to remove the excess terpene from the fibres. It was observed that the fibres produced from the 2% gel stuck together and lost the fibre shape while fibres prepared from 3% gel kept the fibre like form without sticking to each other. It was decided to set level one for the concentration at 3% and level two at 5%. After deciding the factors and levels, an experimental design was conducted to find out the effects of the different factors and their interactions. The experimental design and levels are shown in Table 4.1 and Table 4.2.

Factors	**Low Level**	**High level**
Polymer particle size	150 <X^{*}<250 micron	Y^{λ}>250 micron
Temperature	130^{o}C	150^{o}C
Heating time	1hr	3hr
Concentration	3%	5%

Table 4.1 Factor levels for the terpene extrusion experiment

X^{*} represent the size of the particle which are greater than 150 micron but smaller than 250 microns

Y^{λ} represents the particles size greater than 250 micron

E.No.	R.O	Polymer particle size µm	Temperature ^{o}C	Heating time Hr	UHMWPE Concentration %
1	3	X	130	1	3
2	8	X	130	3	5
3	4	X	150	1	5
4	7	X	150	3	3
5	2	Y	130	1	5
6	5	Y	130	3	3
7	1	Y	150	1	3
8	6	Y	150	3	5

Table 4.2 Experimental design for the terpene experiment

R.O. *Random order in which the experiment was conducted*

E.No. *Experiment number*

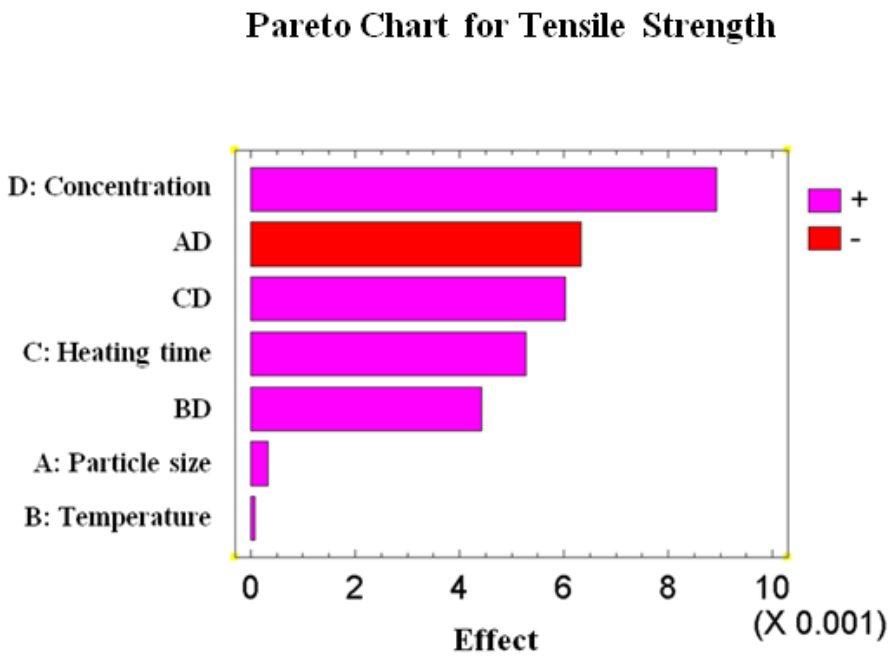


Figure 4.12 Effects of different factors on the tensile strength of fibre

The factors that showed the biggest effect was concentration as shown in the pareto chart in Figure 4.12. The second biggest effect was shown by the combination of particle size and concentration but the –ve plot indicates that low levels of concentration and particle size positively influence the strength of the fibres. The third most important factor was the combination of concentration and heating time followed by heating time and combination of temperature and concentration. The particle size and temperature did not show any significant effect.

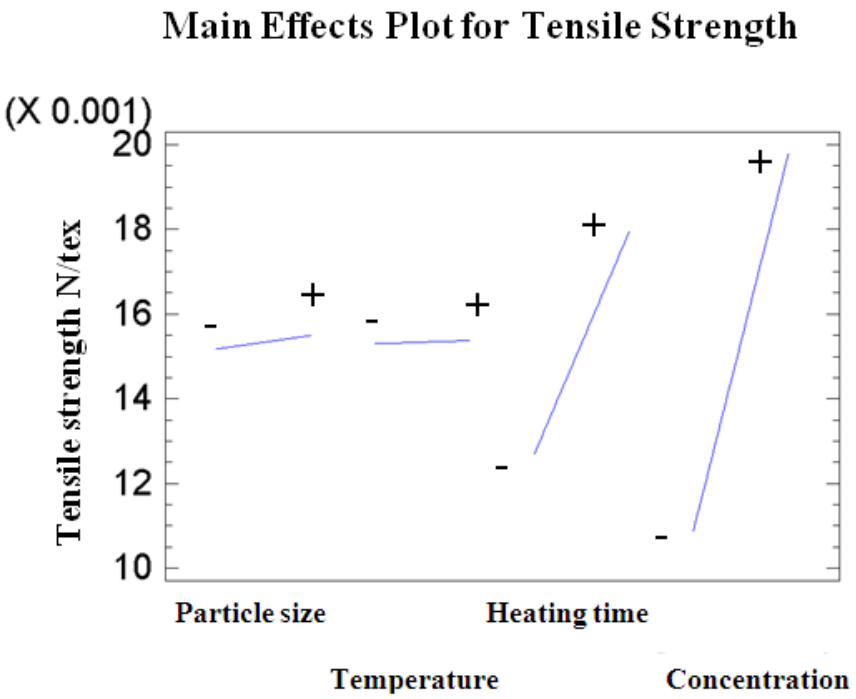


Figure 4.13 Effects of main factors level on tensile strength (-ve represents low level, +ve represents high level)

The plot in Figure 4.13 shows the effect of main factors on tensile strength. In the plot particle size did not show any significant effect on the response. Both levels of particles sizes showed no significant change in response. Temperature also showed no significant effect on the response represented by parallel line to the x-axis. Heating time shows a considerable effect on the response. The low level of heating time gave weaker fibres comparing to high level of heating time which gave stronger fibres. Concentration was found to have the most significant effect on the strength of the fibre indicated by the line along the y-axis.

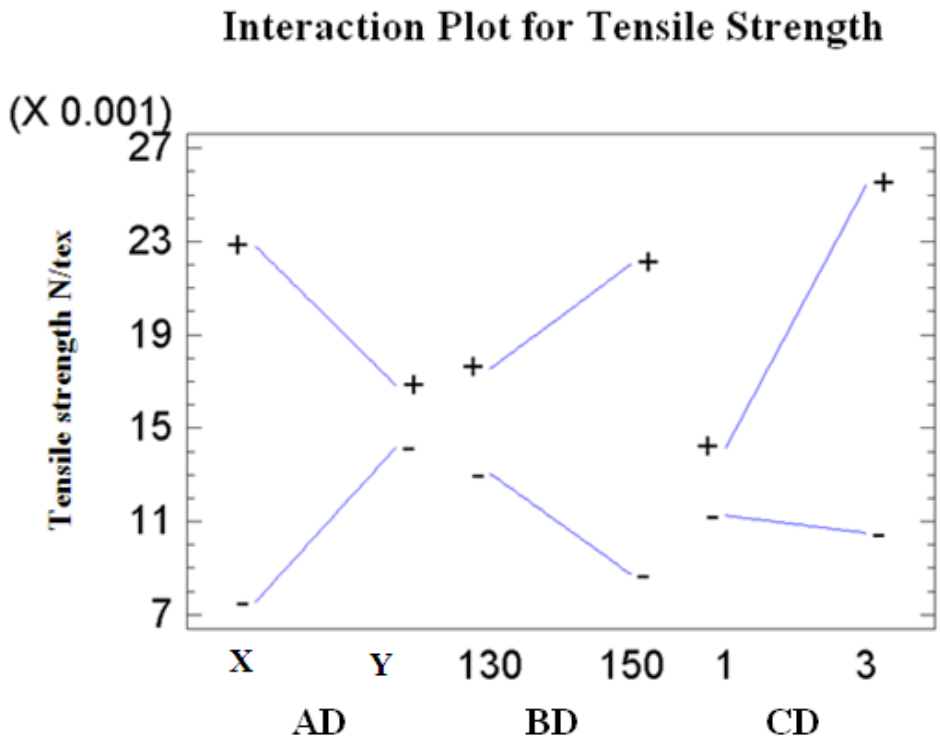


Figure 4.14 Interaction Plot for tensile strength (-ve indicates low level of D and +ve indicates high level of D)

The interaction plot in Figure 4.14 shows very high negative interaction between concentration of the polymer (D) and particle size (A). At lower levels of concentration and particle size the strength is very low. The high level of particle size with low level of concentration gave better response than the previous however, the maximum response values were achieved with high level of concentration and low level of particle size. The other factors which showed the interaction were temperature (B) and concentration (D). At low level of D and high level of B the response value was minimum while the maximum value of the response was achieved with both B and D at high level indicating positive interaction. The heating time (C) and concentration (D) showed very high interaction the maximum response value was achieved with high level of both factors C and D. While at low level of D the heating time (C) did not significantly affected the response.

4.6 Screw Extrusion

The gel spinning of UHMWPE on the ram extruder encouraged further experimentation with the screw extruder, which provides the benefit of continuous extrusion in contrast to ram extrusion. Due to the completely different working principle of the screw extruder, it has its limitations, which needed to be addressed.

One of the most important limitations was the MFI of the polymer; a screw extruder cannot extrude polymer with very low MFI as was possible with ram extrusion. The MFI of UHMWPE is relatively low (<0.1 g/10 min). To investigate the potential of screw extrusion of terpene gel the MFI of the gel was measured. The measurements provided the range of MFIs between 4-5 g/10 min. It was found the MFI is greatly dependent on the concentration of the polymer in the gel.

To extrude the gel on a screw extruder, gels were prepared by heating 5% w/v of UHMWPE in terpene with 1% ionol and 1% aluminium stereate at 130^{o}C for 1 hour. These conditions were found to be optimum in the previously conducted experimental design. The gels were left overnight to cool down to room temperature. The gel at room temperature was converted into the form of chips (approx 3×3 mm). The gels for all screw extrusion experiments were prepared in the same way. The chips were fed into the screw extruder (see chapter 3). The conditions at which the extrusion was conducted are given in Table 4.3.

Extruder			Pump	Die head	
Zone 1	Zone 2	Zone 3		Zone 1	Zone 2
100^{o}C	130^{o}C	150^{o}C	150^{o}C	150^{o}C	150^{o}C

Table 4.3 Heating profile of the Screw extruder

The extrusion of the gel on the screw extruder gave an uneven filament. The reason was thought to be excess terpene in the chips causing slippage resulting lower back pressure from feed. In order to overcome this problem it was decided to reduce the amount of terpene in the gel by drying. As discussed previously, the MFI of the gel was found to be dependent on the concentration of the polymer in the gel. Hence, it was necessary to find an optimum drying time to keep the MFI above 4 g/10 min. In order to find the optimum drying time, the gel chips were dried in an oven at 25^{o}C. MFI of the gel chips was measure after every 12 hours. The time of 24 hr drying was found to be the optimum length of time to keep the MFI above 4 g/10 min.

The same experiment was repeated with dried chips. However, the experiment with dried chips also resulted in a lack of uniformity, which was observed to be related to the feed of the gel chips through the screw. To overcome this problem, experiments

were run with a different temperature profile as shown in Table 4.4. The maximum temperature was set at 150^{o}C to avoid evaporation of terpene. The temperature in the extruder was increased with different profile as its well known the temperature profile affects the extrusion process.

Extruder			Pump	Die head	
Zone 1	Zone 2	Zone 3		Zone 1	Zone 2
50^{o}C	80^{o}C	130^{o}C	130^{o}C	150^{o}C	150^{o}C
80^{o}C	130^{o}C	140^{o}C	150^{o}C	150^{o}C	150^{o}C
100^{o}C	130^{o}C	140^{o}C	150^{o}C	150^{o}C	150^{o}C

Table 4.4 Temperature profile of screw extruder

The screw extrusion of the gel was not found to be sensitive to temperature profile. It was observed that the chips were compacting due to the screw rotation. This compaction of the gel was adversely affecting the back pressure. Figure 4.15 and Figure 4.16 show the compaction of gel on the screw extruder.

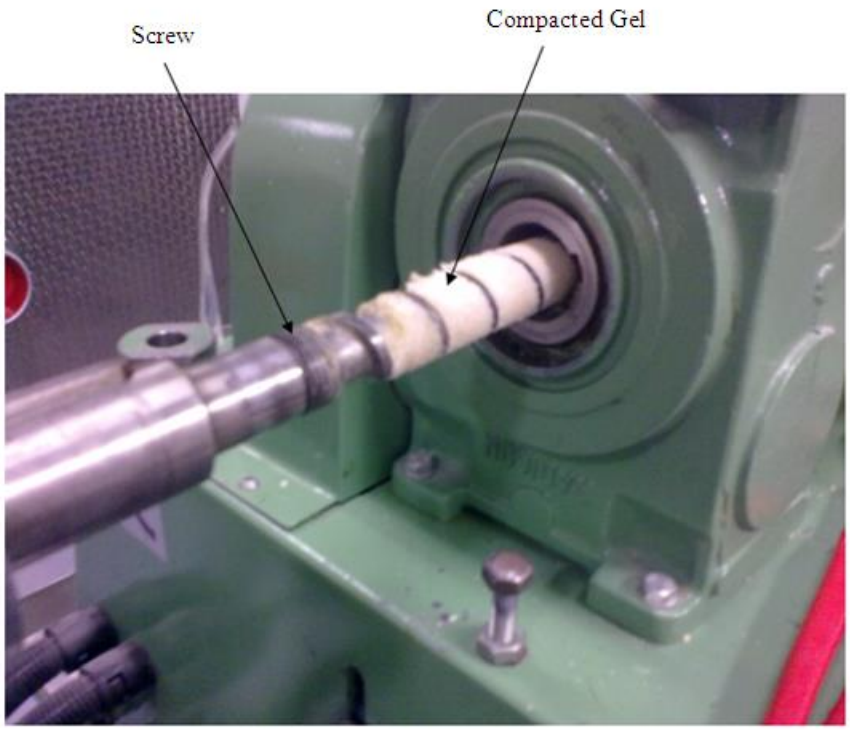


Figure 4.15 Gel compaction on the screw

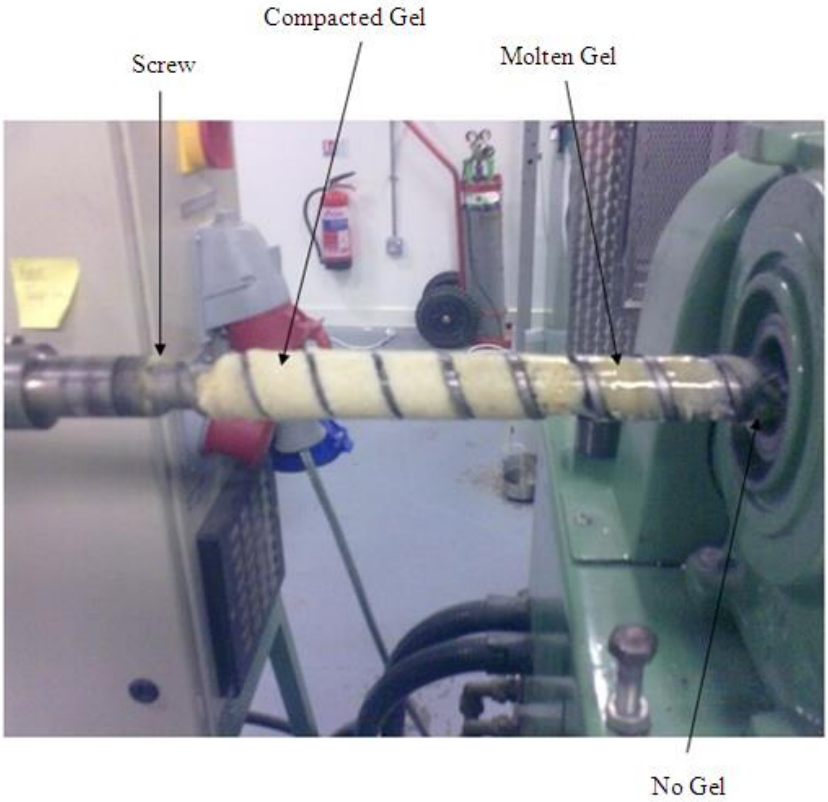


Figure 4.16 Gel compaction on the screw

Due to this compaction on the screw, the feeding of the polymer was not possible. The reason for this compaction appeared to be the compression zone of the screw indicated in Figure 4.17. The screw contained three main zones characterized by the depth of the channel. The first zone had a deeper channel which conveyed the polymer forward to the compression zone which had shallower depth. The shallower depth gave higher friction hence creating more heat, which melted the polymers. The third zone of the screw was the metering zone which had a shallower but constant channel. In the melt extrusion of the polymers the feeding zone generates enough pressure to move the polymer forward through the compression zone. In the case of the gel extrusion, due to the soft nature of the gel, rather than generating pressure to move the gel through the compression zone, compaction occurred as shown in the schematic diagram in Figure 4.18. This compaction of the gel clogged the screw making extrusion impossible. Thus, all experimentation on the screw extruder was abandoned due to unavailability of an appropriate screw.

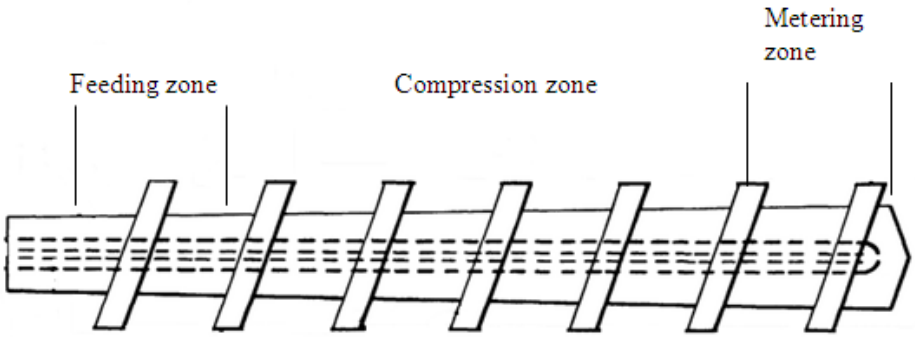


Figure 4.17 Different zones of a typical Screw

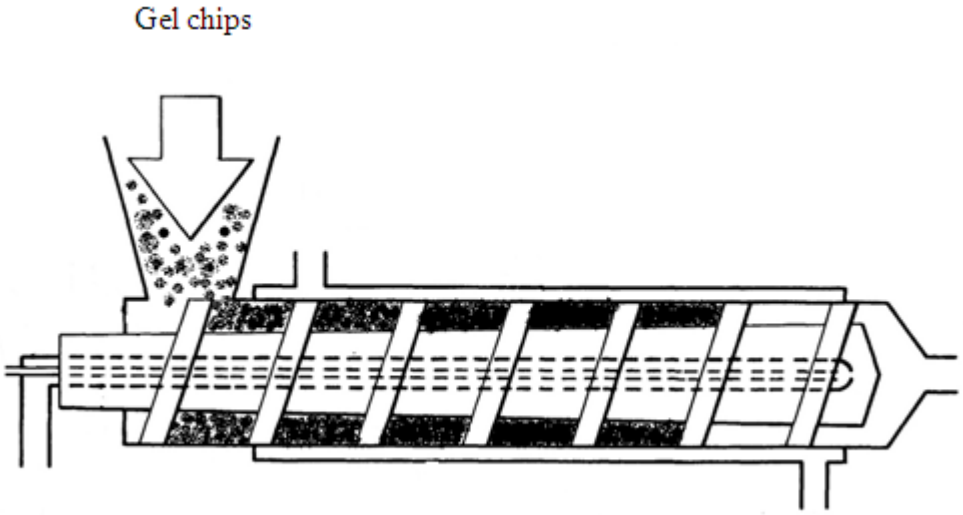


Figure 4.18 Compaction of chips inside the extruder

4.7 Ultrasonic Treatment

The fifth objective of the research was to investigate the effect of the ultrasonic treatment for the improvement of polymer chain alignments. A setup was designed to treat the UHMWPE gel with ultrasound before extrusion. Ultrasound has been extensively used in the preparation of homogenous polymer solution in the past [100] however, the effect of ultrasound treatment on gel spinning has not been reported in the literature one of the reason could be the phase separation of the UHMWPE polymer solution. The ultrasonic bath contains water which cannot be heated above 100^{o}C while UHMWPE polymer solutions needs to be kept at 130^{o}C to avoid phase separation. A

setup was designed shown in Figure 4.19 to treat the polymer solution with ultrasound. The gel was prepared by heating 5% w/v solution of UHMWPE and terpene at 130^{o}C for one hour. The beaker was then put in an ultrasonic bath containing paraffin oil. Paraffin oil was chosen instead of water, as the boiling point of the paraffin is considerably higher than the water. The gel was required to be maintained at 130^{o}C, which was not possible with water. The Ultrasonic bath was maintained at 130^{o}C by placing a submergible heater in the ultra sonic bath as shown in Figure 4.19. The gel was kept in ultrasonic bath for 30 min.

Figure 4.19 Ultrasonic treatment setup for UHMWPE gel

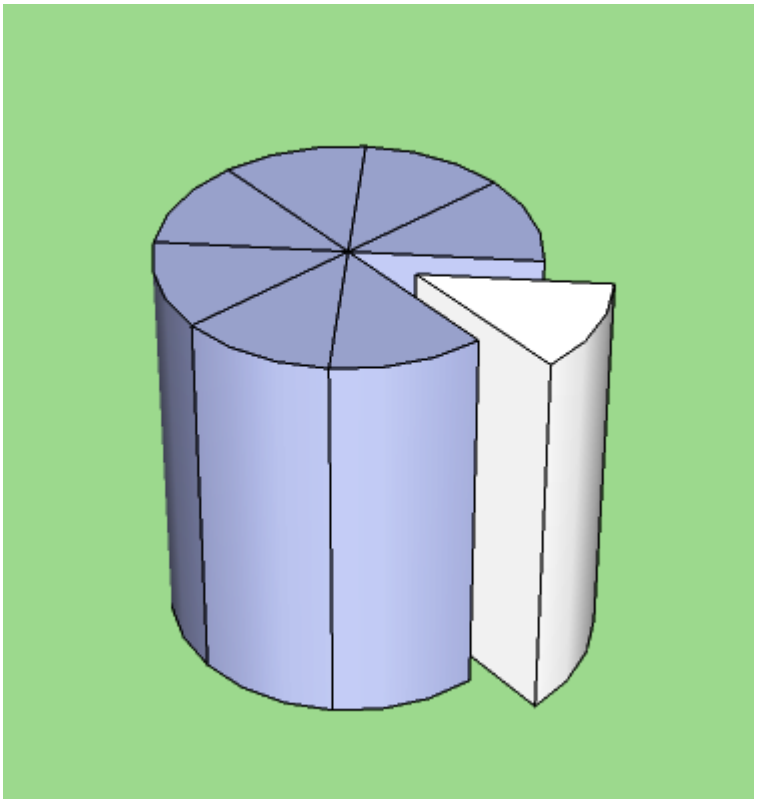


Figure 4.20 Gel pieces cut along the axis of the beaker

The gel was left overnight at ambient temperature and then cut into large pieces along the axis of the beaker (approx 10 cm by 3 cm V shape similar to cake cut Figure 4.20). Since the purpose of the ultrasonic treatment was to disentangle and align the polymer chains. It was necessary to cut the gel in the above mentioned pattern in order to retain the alignment of polymer in one direction, which can easily be lost if the gel was cut in random direction. The pieces were then fed into the ram extruder. The extrusion was performed at 150^{o}C. The gel pieces were left in the ram barrel for 10 min to heat the gel uniformly. The extrudate was passed through an air gap followed by quenching in water at room temperature and winding. The fibres were left to dry at room temperature.

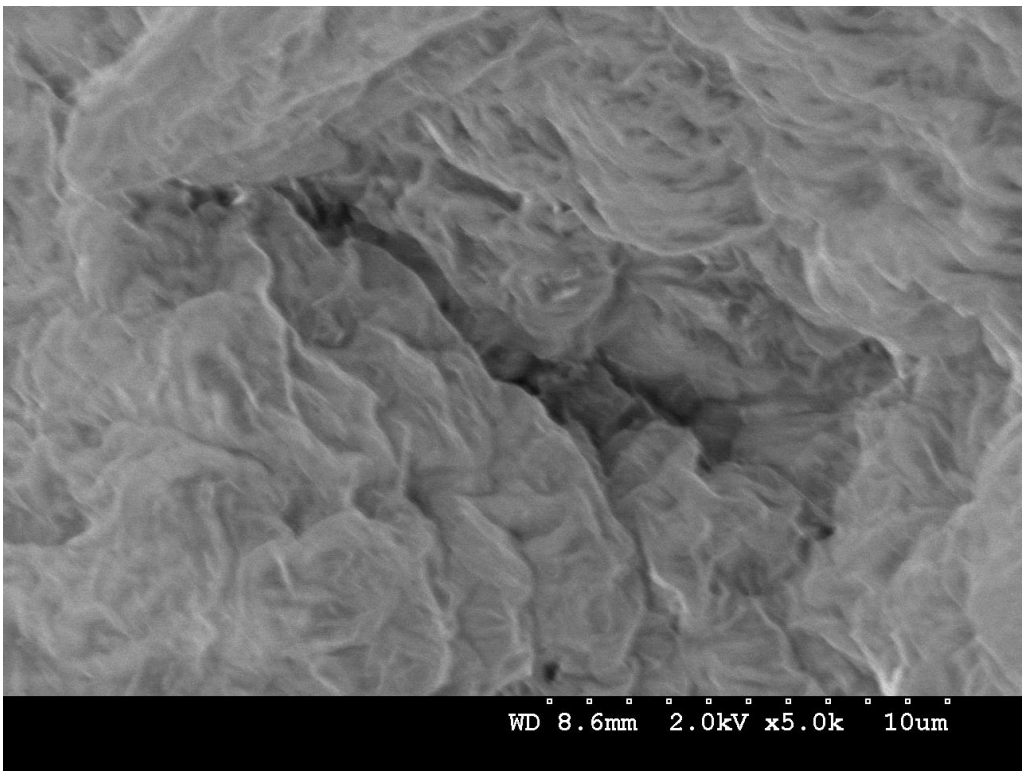


Figure 4.21 SEM image of untreated gel

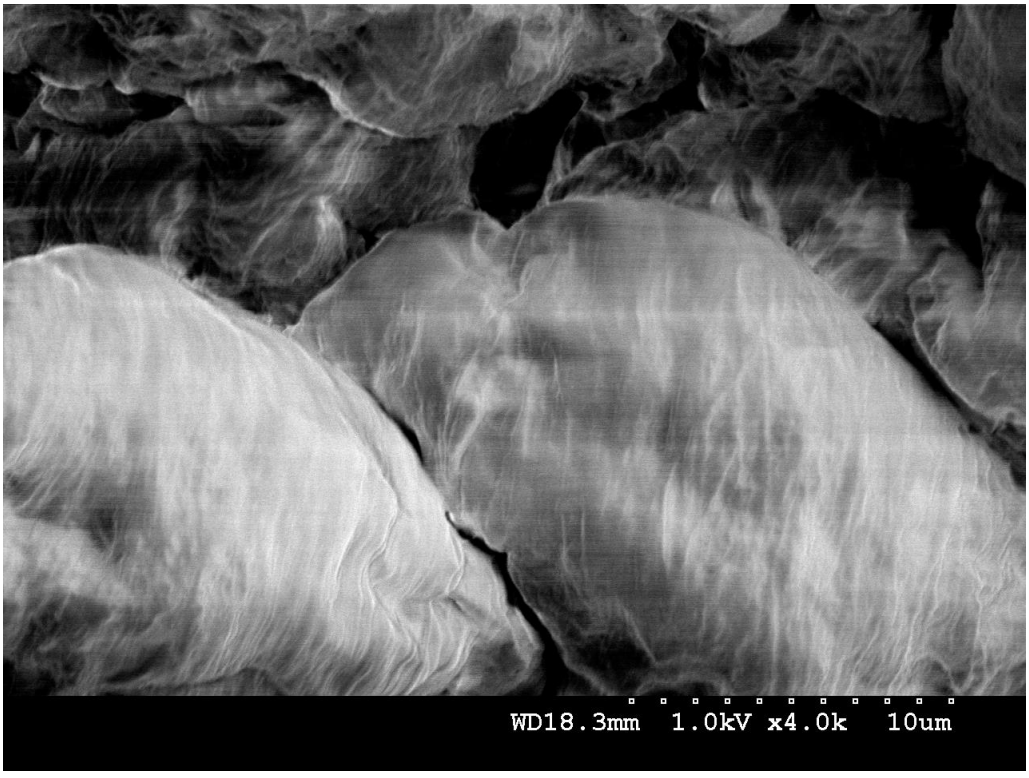
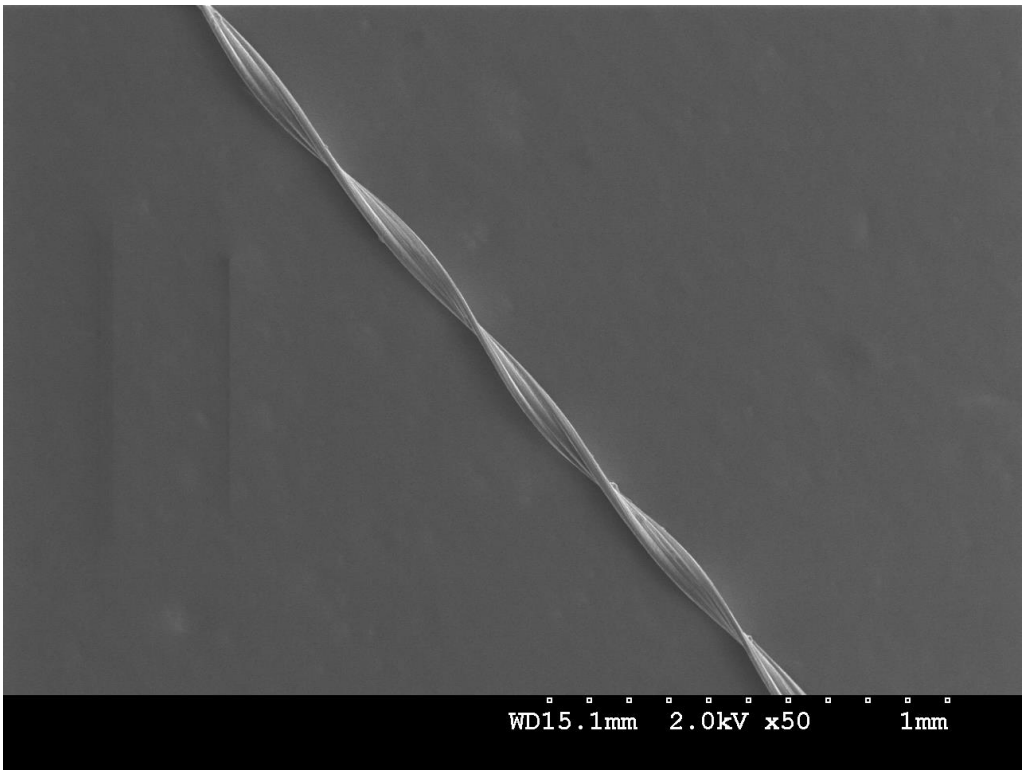


Figure 4.22 SEM image of ultrasonic treated gel

The SEM images of treated and untreated gel were taken shown in Figure 4.21 and Figure 4.22. The SEM images of untreated gel showed no particular direction of the fibrils rather the fibrils are random in direction as indicated in Figure 4.21, while the gel treated with ultrasonic energy showed fibrils aligned in one direction as shown in

Figure 4.22. This alignment of fibrils reduces the chance of entanglements while the random direction of fibrils as shown in the Figure 4.21 causes the entanglements and creates weak places in the fibres.



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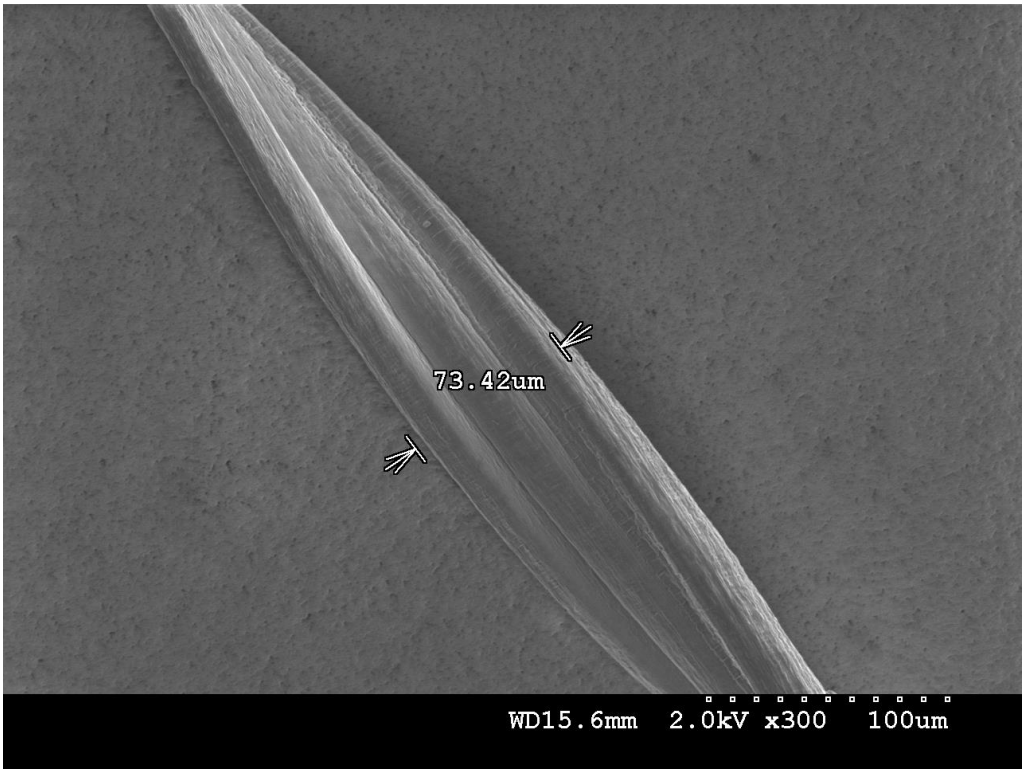

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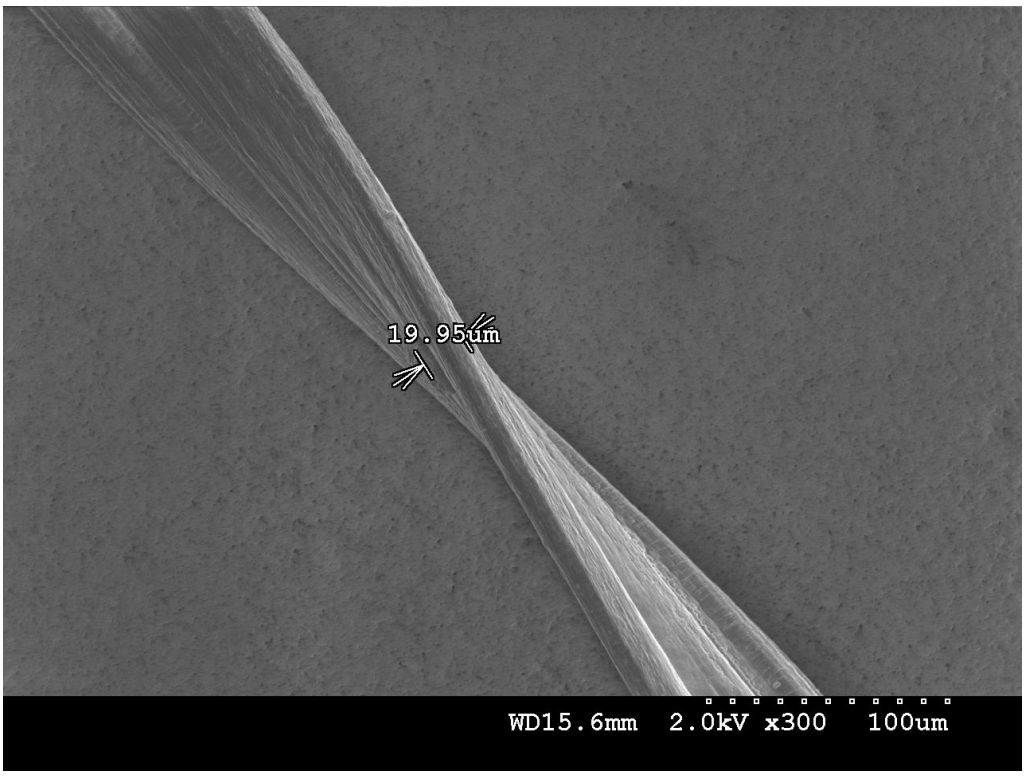

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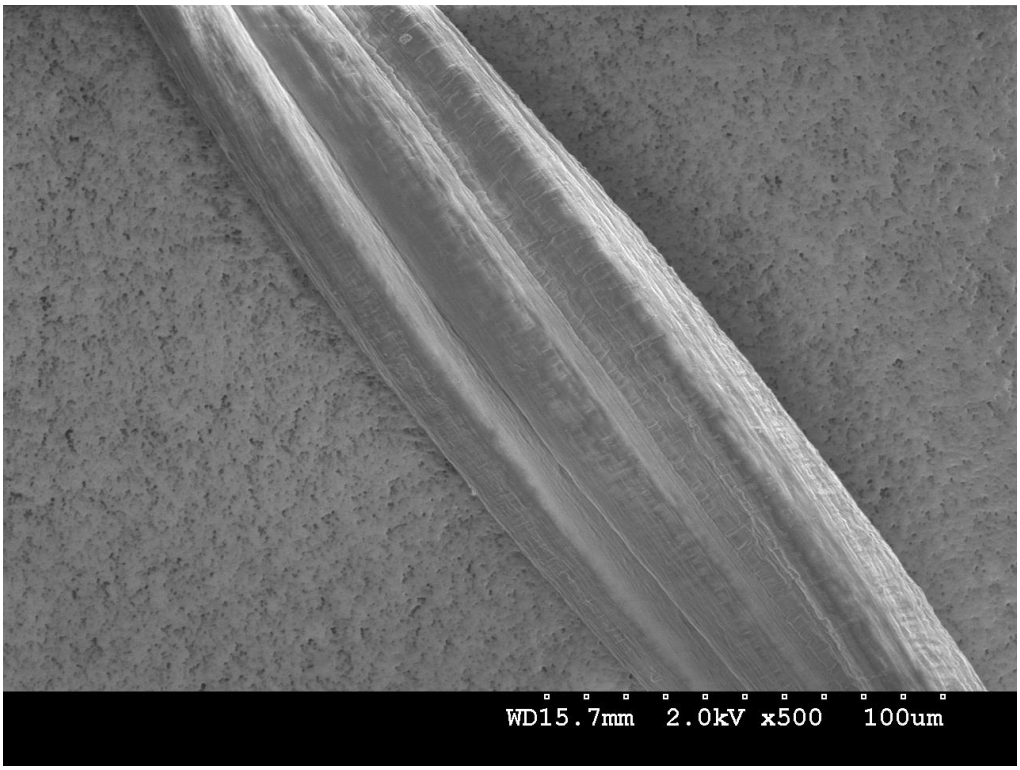

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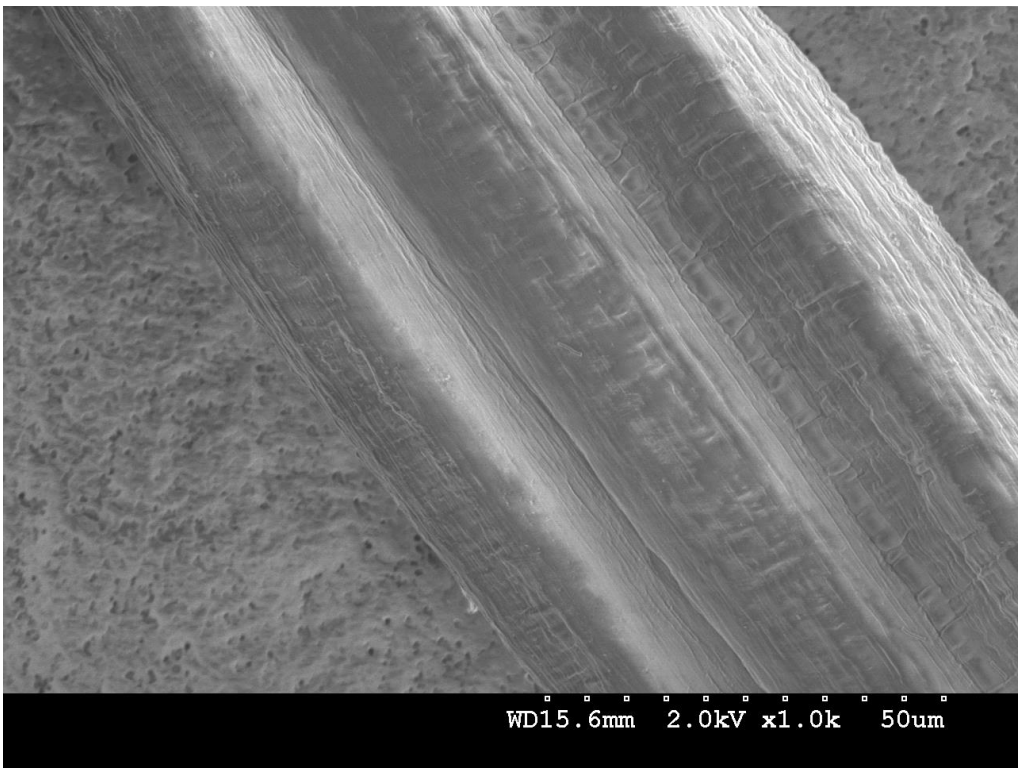

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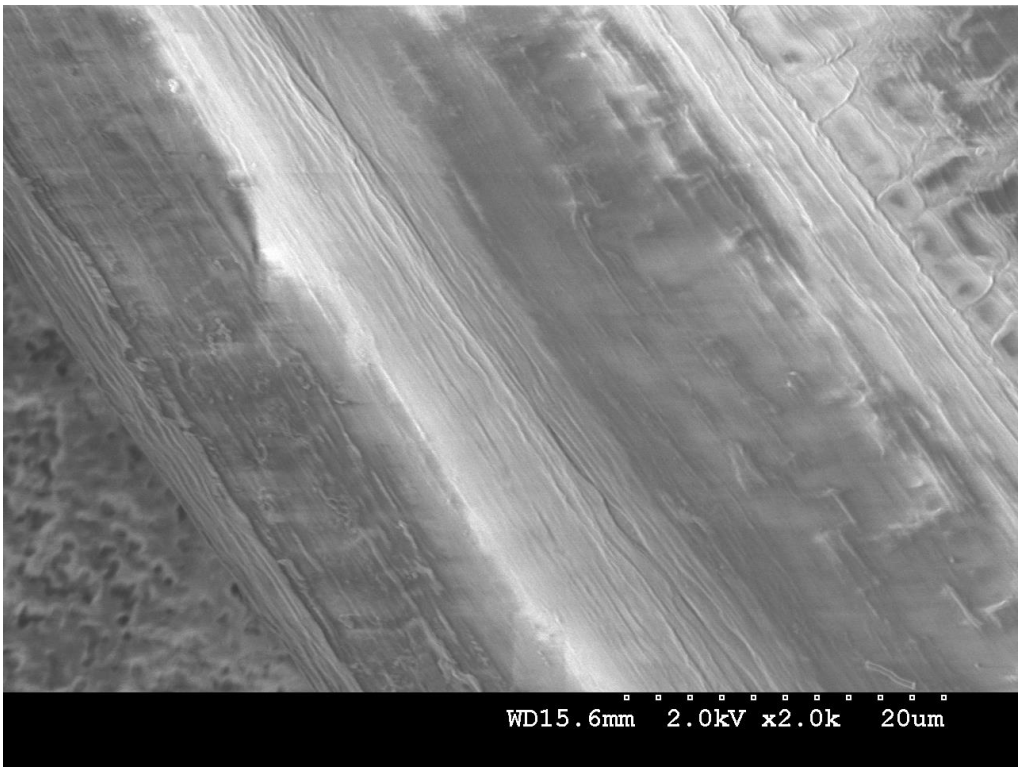

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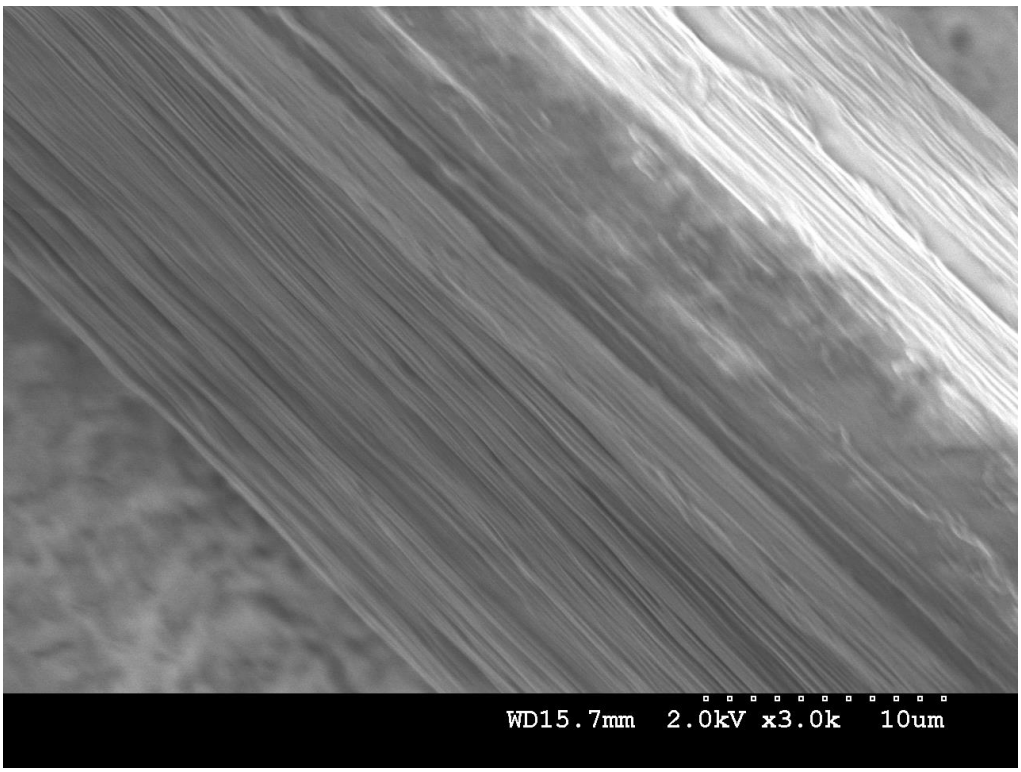

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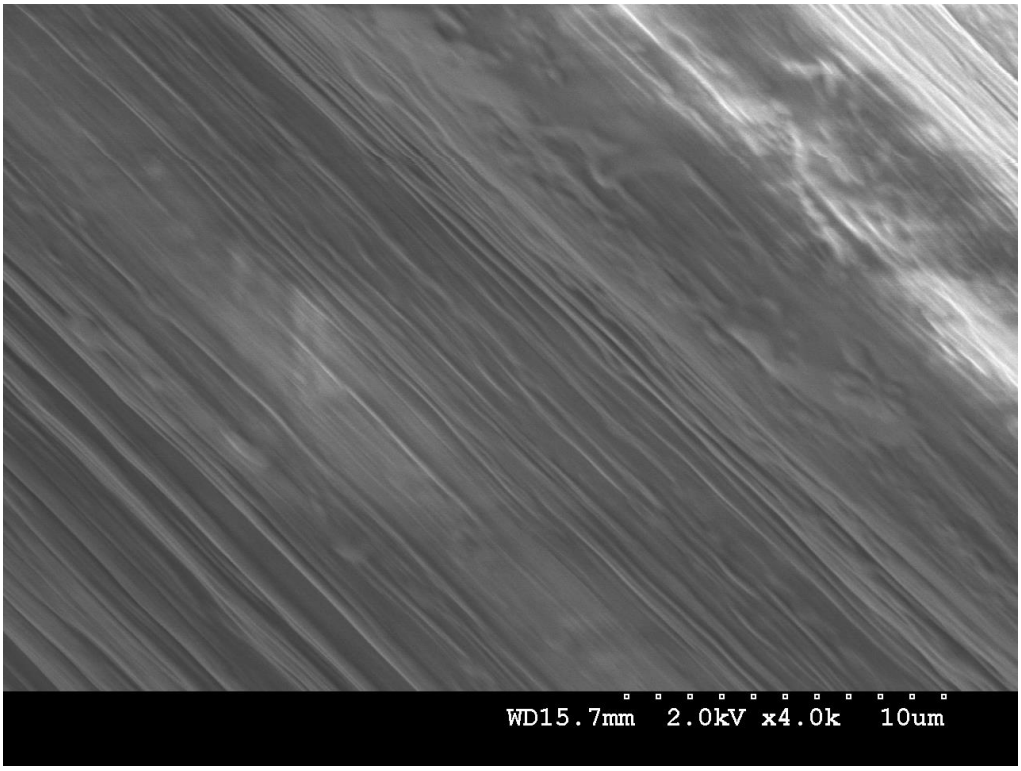

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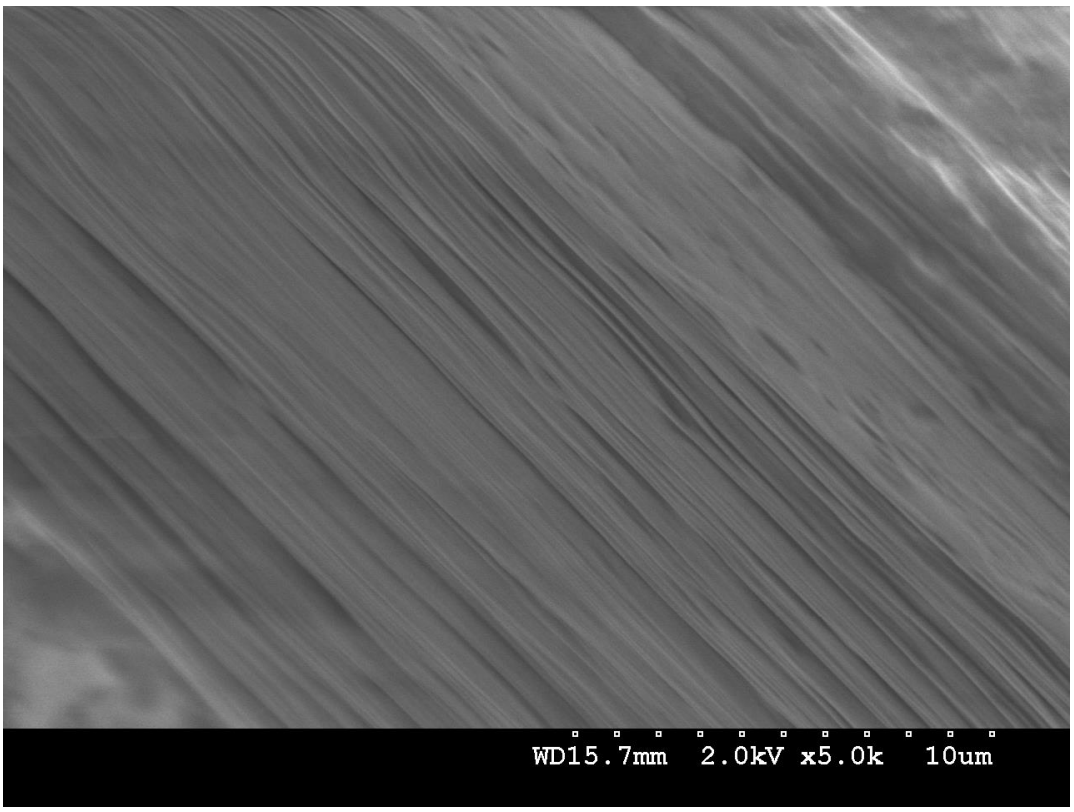

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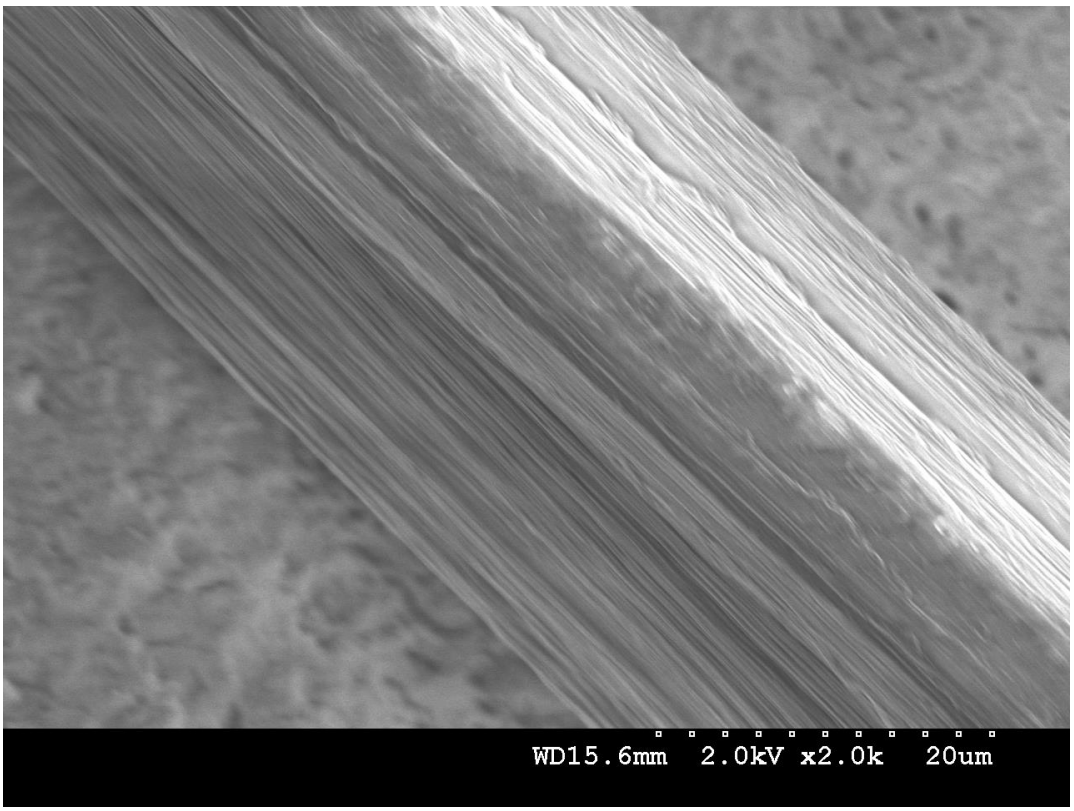


j

Figure 4.23 SEM images of ultrasonic treated UHMWPE Fibres

The ultrasonic treated fibres were found to be consistently uniform and one discovery of note was the shape of the fibres' cross section. The fibres were found to be ribbon shaped containing three rod-like sections as shown in Figure 4.23 (a-e). Since the extrusion was performed with a circular die, the ribbon-like structures cannot be due the shape of the die. Prevorsek [4] reported that the shape of the fibres could differ greatly depending on the solvents used to remove the solution from the fibres. He explained that the shape of the fibres varies progressively from a smooth cylindrical shape in proportion to the boiling point of the extracting solvent i.e. the fibres extracted with diethyl ether had a close to cylindrical shape while the fibres extracted with toluene were C-shaped. In the present study no extraction solvent was used and the extraction was achieved by the combination of the water quenching and drying at room temperature. This unique method of solvent extraction can be responsible for the cylindrical rod like shape of the fibre. As the extraction method was the same for all the experiments, the flat ribbon like shape was not observed in the fibres extruded with untreated gel. The reason for the flatness of the fibres was the extreme lateral force experienced by the extrudate during the quenching generated due to the winding force and lack of output from the die head. Since the extrudate encountered the roller in the water bath, the combination of forces generated by the winding and lack of output from the die head were responsible for the flat shape of the fibres. The fibrils of ultrasonic treated fibres were found to be consistently uniform and align in the same direction as shown in Figure 4.23 (f-j).

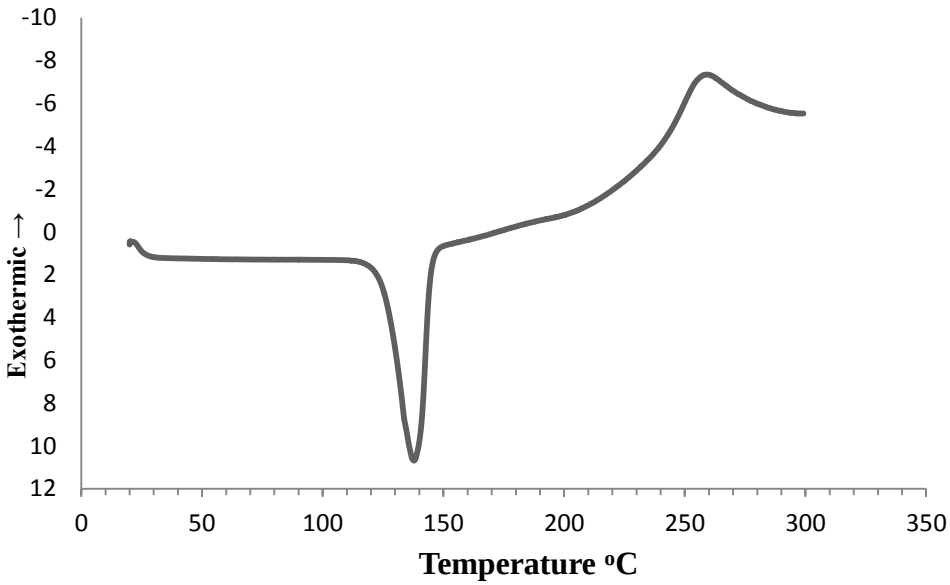


Figure 4.24 DSC thermograph of ultrasonic treated UHMWPE yarn

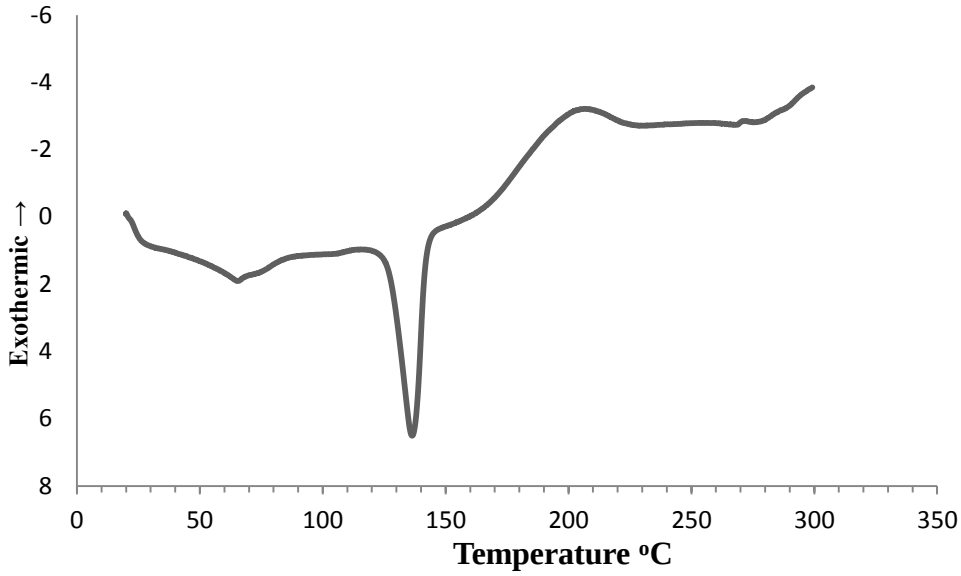


Figure 4.25 DSC thermograph of UHMWPE yarn

The DSC thermographs of untreated and treated fibres differed from each other as the treated fibres showed a smoother line while the untreated fibres demonstrated uneven line (see Figure 4.24 and Figure 4.25). This unevenness in the untreated fibres was due to the presence of the defects e.g. folds, trapped entanglements, kink, jog, chain end twist, wedge etc in the fibre structure. The ultrasonic treated fibres showed a small increase in the melting peak indicting the reduction of defects and increased crystallinity.

The strength of the ultrasonic treated and untreated fibres was tested and compared to the previously reported strength which is shown in Table 4.5.

Sample	**Fibre linear density (tex)**	**Strength (N/tex)**	**Maximum load (N)**
Untreated fibres	23	0.026	0.598
Ultrasonic treated fibres	1.3	0.169	0.22
As spun fibres (reported by Smith et.al)		0.096	

Table 4.5 Comparison of tensile strength of as spun fibres and ultrasonic treated and untreated fibres

The strength of untreated, ultrasonic treated and previously reported as spun fibres are compared in Table 4.5. The strength reported by Smith et. al. of as spun fibre is 0.096 N/tex while the strength of the untreated fibre achieved was lower [39]. However, the fibres treated with ultrasonic energy showed significant improvement in the strength. The strength of the treated fibre is about 1.5 times more than the previously reported fibres strength. This is due to the higher molecular weight polymer grade. The polymer grade reported by Smith et. al. was 1.5×10^6 g/mol while in the present study the polymer grade used was 5.0×10^6 g/mol. However, the higher strength can not only be reason of higher strength since the untreated fibres were also produced by the same grade of polymer but showed lower strength which is also due to higher molecular weight which give rise to entanglements thus weaker fibres. The higher molecular weight can only be of advantage if the entanglements are reduced. In the

case of ultrasonic treated fibres these entanglements get disentangled thus results in the stronger fibres. To further investigate the disentanglement effect of the ultrasonic treatment the orientation of the fibres were tested.

The orientation of the fibre polymer is an important factor when discussing the physical properties of the fibres. In the absence of the other inter-molecular forces in UHMWPE the Van de Waals' are the most important inter molecular forces. Van der Waals' forces are only effective when the polymer chains are very close to each other. Hence, the polymer chains needs to be aligned for Van der Waals' forces to be effective. To investigate the effect of ultrasonic treatment on the orientation, a test was conducted by using three samples, B and C were treated with ultrasonic while the third sample A was untreated. All samples were prepared in the same manner, but samples B and C were treated in the ultrasonic bath for half an hour at 130^{o}C. The extrusion of samples A and B was performed at 150^{o}C while sample C was extruded at 170^{o}C. Each sample was drawn to different ratios as follows DR= 1 (as spun), 2, 3, 4, and 5.

The molecular orientation was determined via the orientation factor (F) equation 4.2.

$$\mathbf{F = \Delta n/\Delta n_o} \qquad (4.2)$$

which was calculated by measuring the birefringence (Δn) of fibres using the interference polarising microscope.

$$\mathbf{\Delta n = Z\lambda/bA} \qquad (4.3)$$

where, Z - the area enclosed under fringe shift

λ - the wavelength used (550nm)

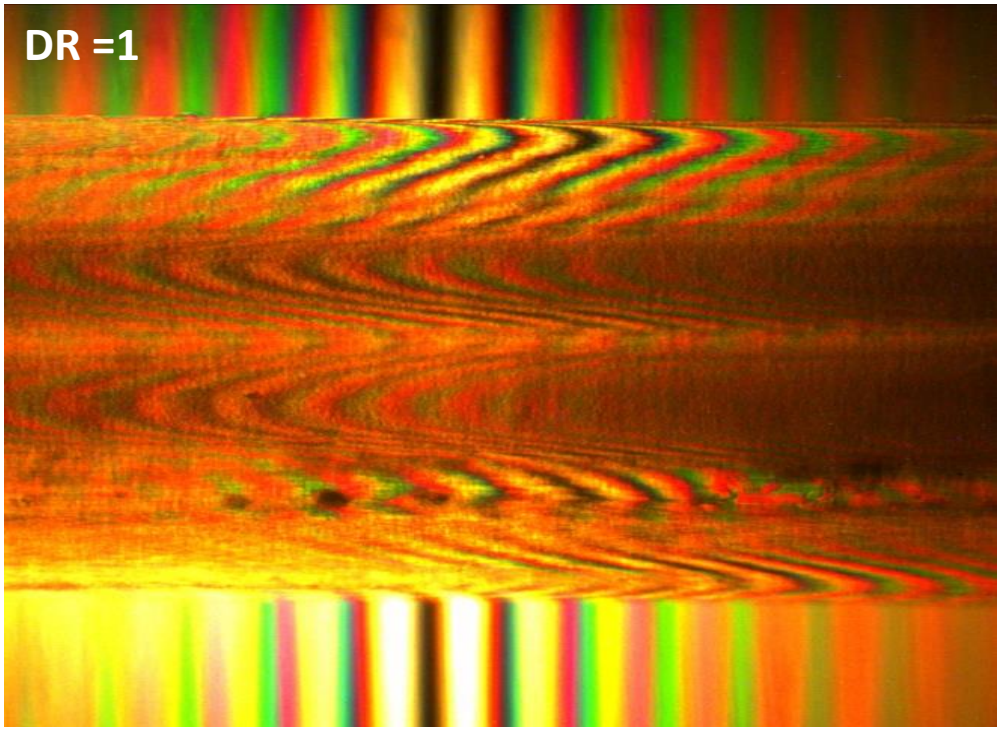
b - interfringe spacing

A – Cross sectional area of the fibre

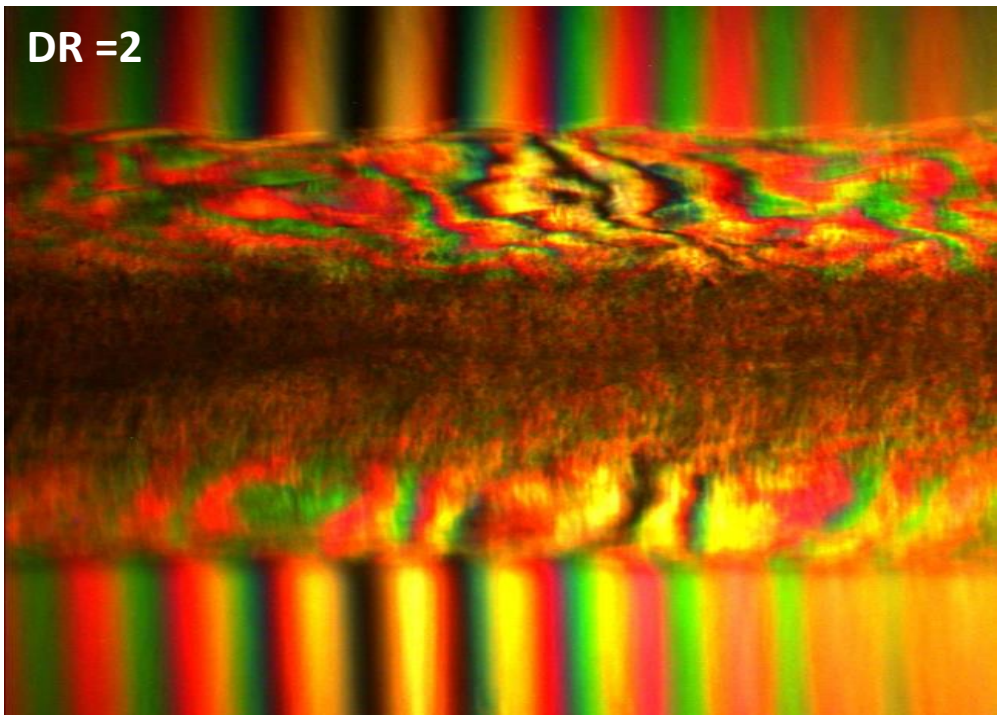
Δn_o – intrinsic/maximum birefringence of fibre, in case of PE fibres,

$\Delta n_o = 0.064$ [109]

Orientation factor is measurement of the alignment of polymers chains. It is measured by dividing the birefringence values of the sample by the birefringence value of the completely oriented polymer. Birefringence is a property of anisotropy crystal material which causes the light to split. The birefringence of the material depends on the alignment of the crystals in the material thus; a material having aligned crystals will show birefringence. The amount of birefringence depends on the degree of alignment of crystals in the material. Hence, the ration of the birefringence of a given sample to birefringence value of the same material having ideal alignment gives the orientation factor showing how aligned is a material. Same phenomenon is used to find the orientation of the fibres. The birefrengance value of a fibre is compared to a value of an ideally oriented fibre of the same polymer which is $\Delta n_o = 0.064$ in case of polyethylene.



a



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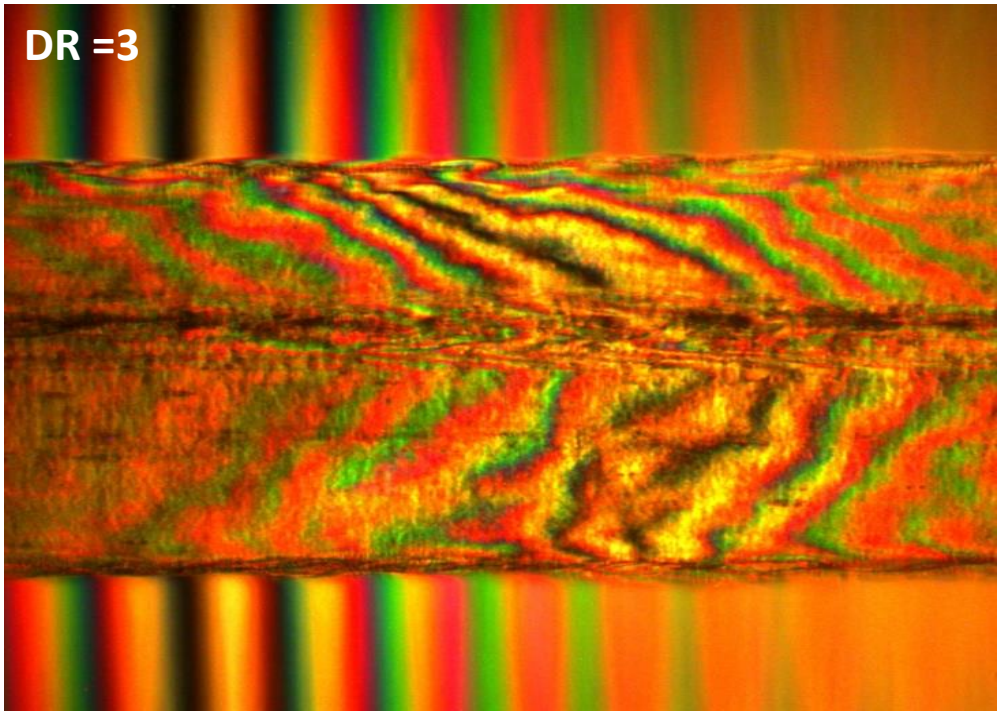

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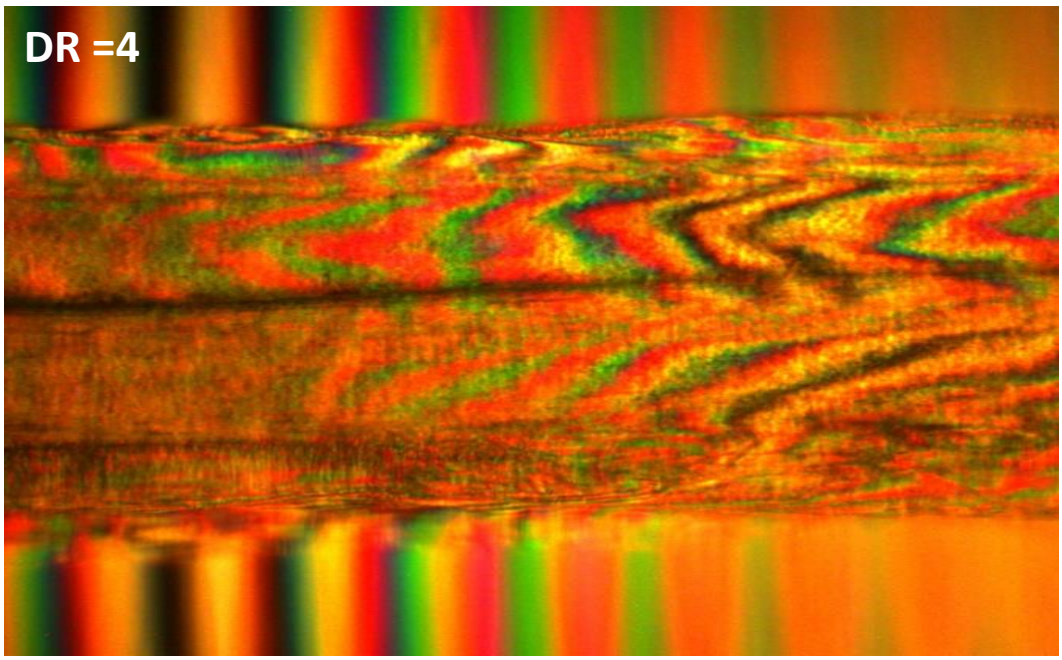

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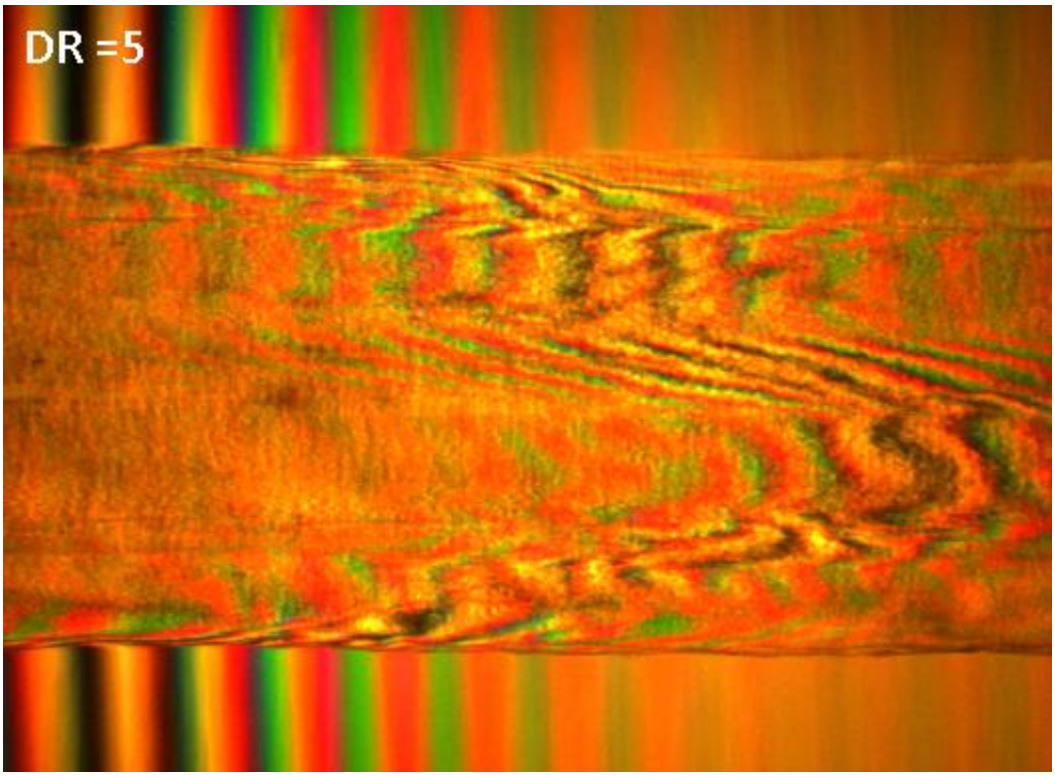
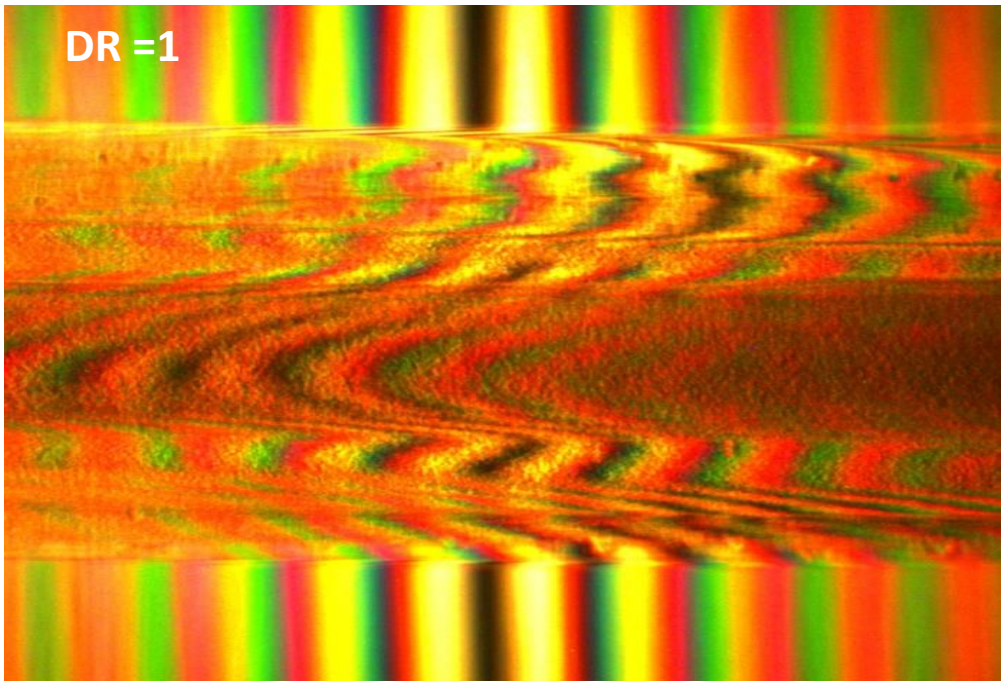


e

Figure 4.26 Microinterferograms of Sample A

The as spun fibre shown in Figure 4.26(a) shows no birefringence the light passes through the fibre without any birefringence while in the fibre drawn to 2:1 shown

in the Figure 4.26(b) slight birefringence was observed. The fibre drawn to the 3:1 shown in Figure 4.26(c) showed better birefringence than the both previous fibre samples. The increase in the birefringence with the increase in draw ratio was also evident in Figure 4.26(d). The microinterferogram of the sample drawn to 5:1 showed the better birefringence than all other samples shown in Figure 4.26(a-d).



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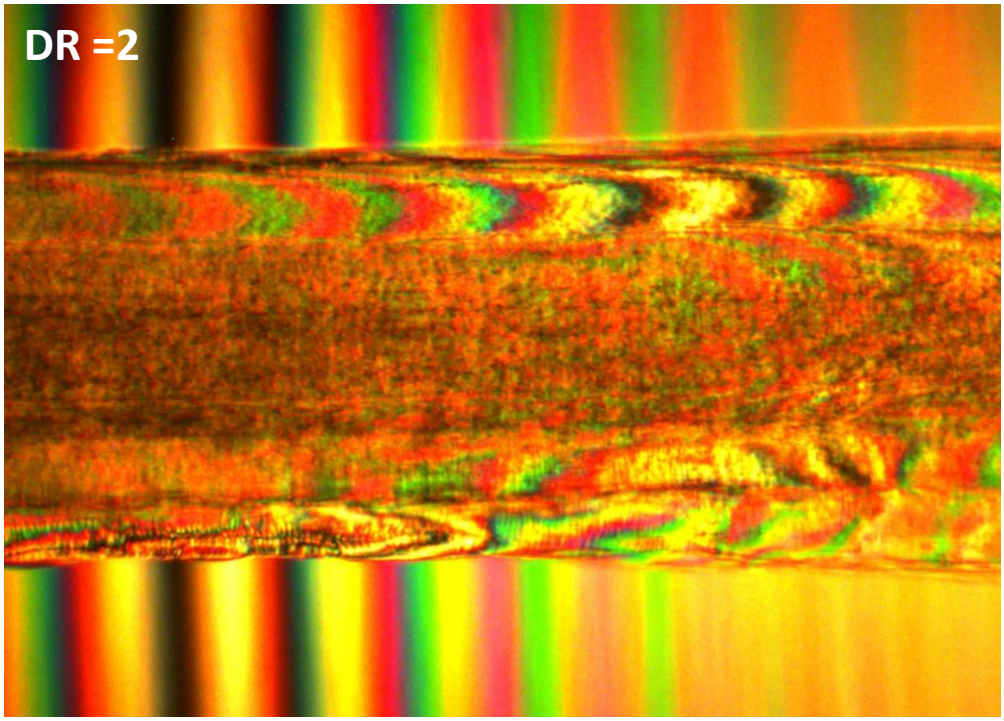

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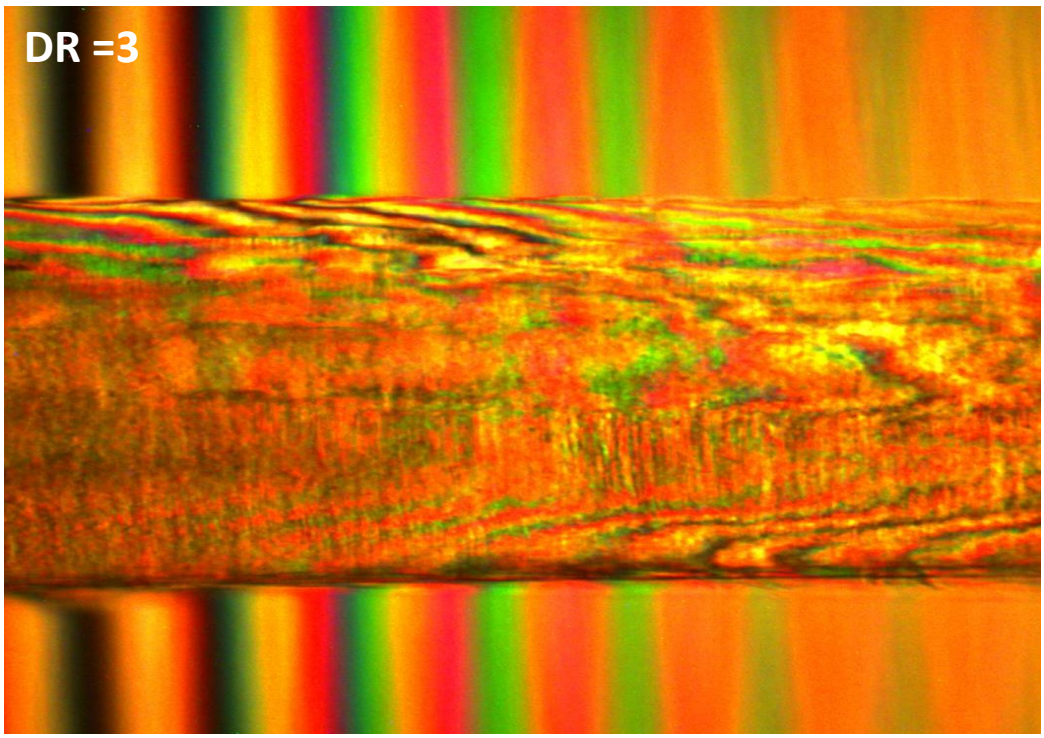

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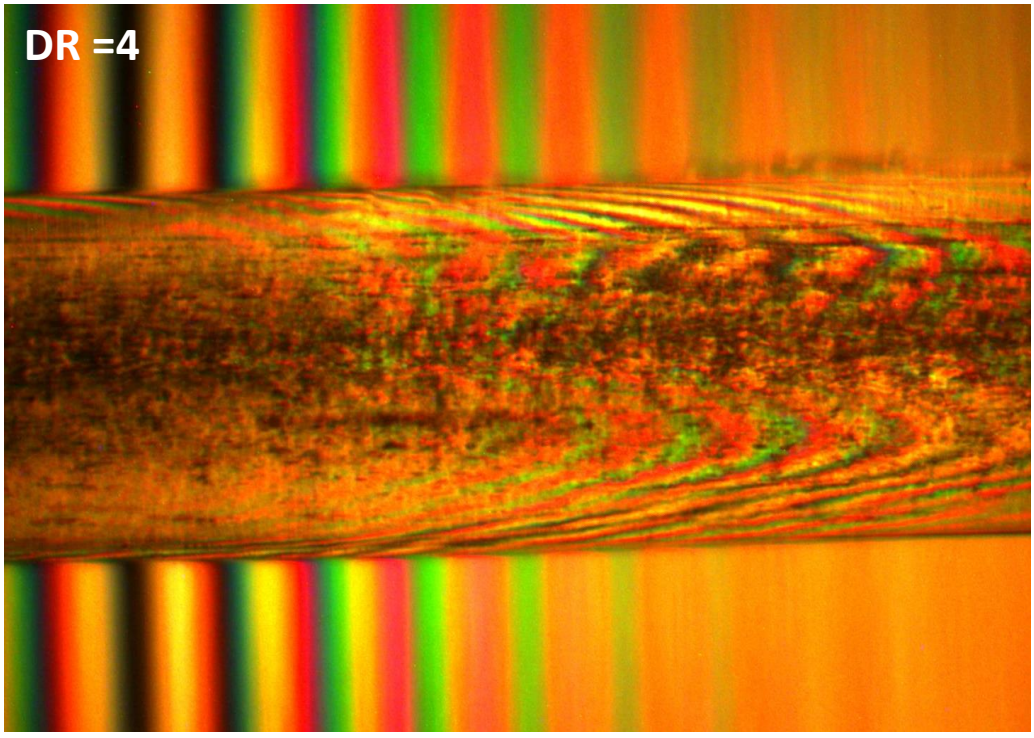

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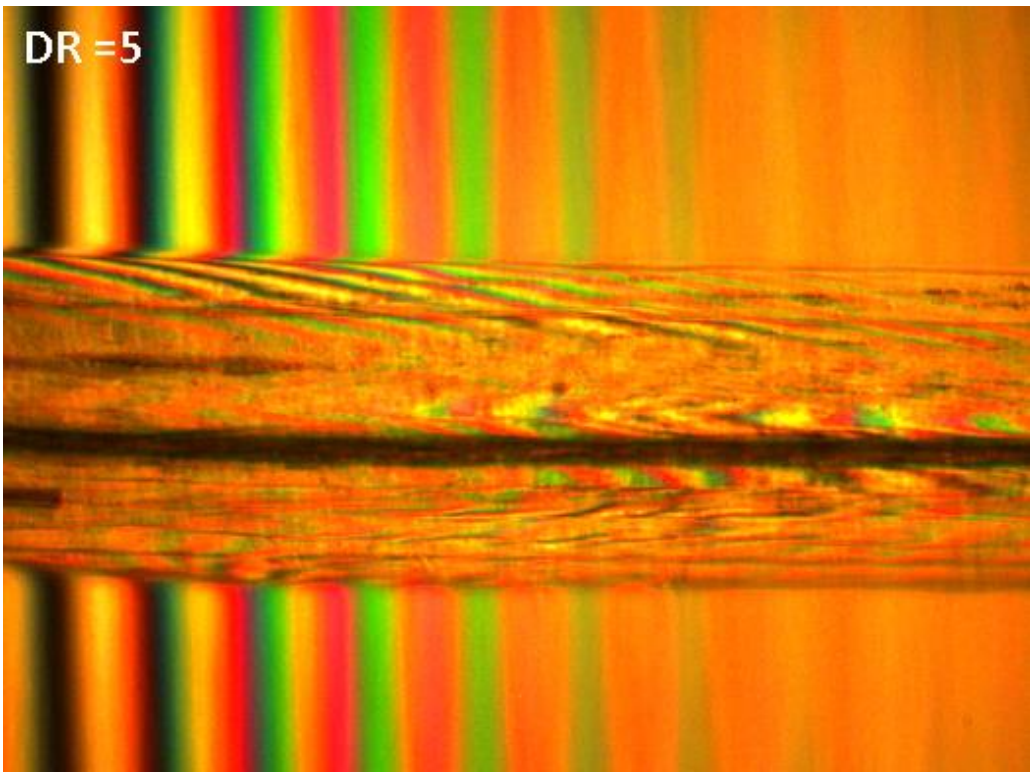

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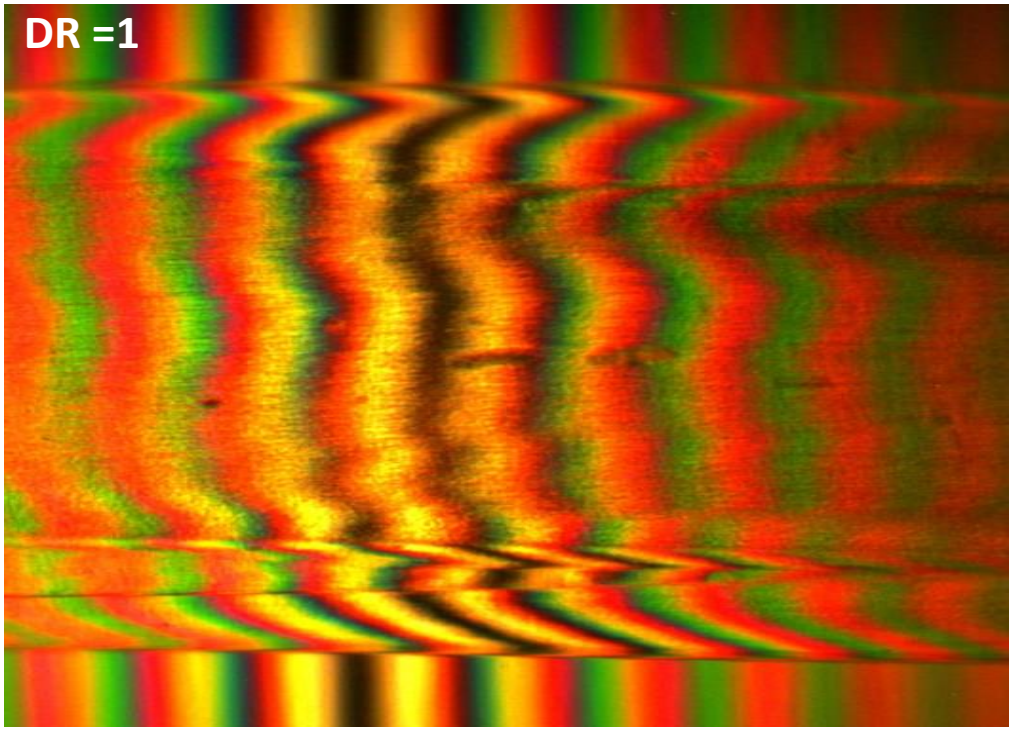
Figure 4.27 Microinterferograms of Sample B

The microinterferogram of the as spun fibre of sample B shown in Figure 4.27(a) indicated no birefringence indicating very low polymer alignment. The drawing of as spun fibre to 2:1 improved the orientation of the polymers indicated by the slight increase in the birefringence shown in Figure 4.27(b). The birefringence further improved in the fibres drawn to the 3:1 ratio shown in Figure 4.27(c). Moreover the fibres drawn to 4:1 shown in Figure 4.27(d) showed further improvement in the alignment of polymers shown by improved birefringence. However the fibre drawn to 5:1 shown in Figure 4.27(e) indicated the biggest birefringence indicating the better alignment of the polymer crystals.



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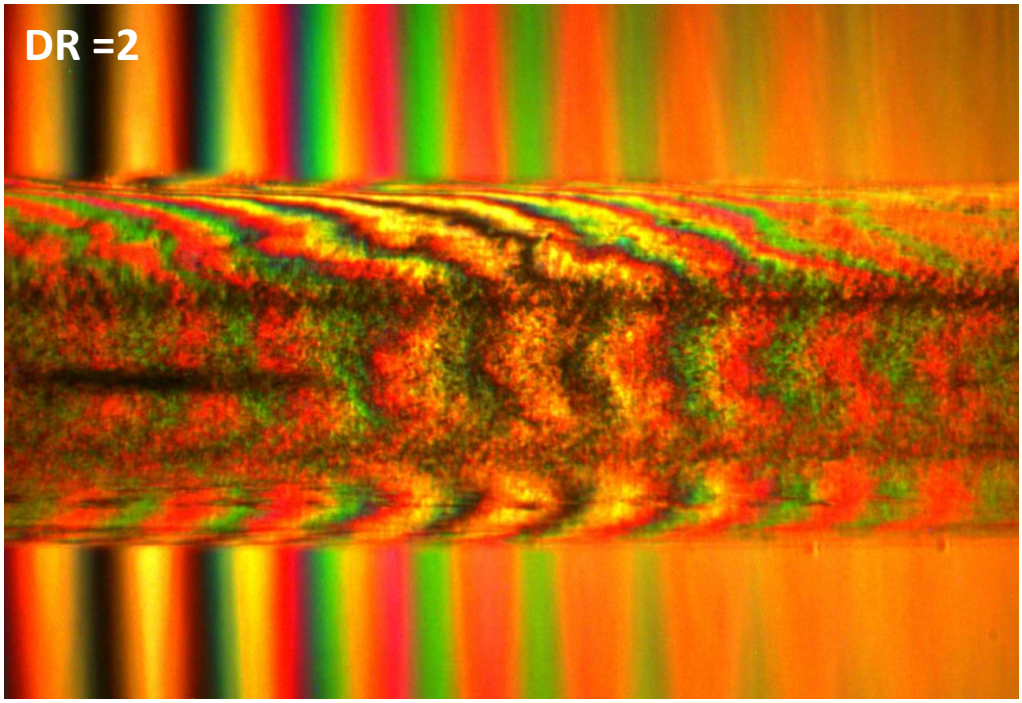

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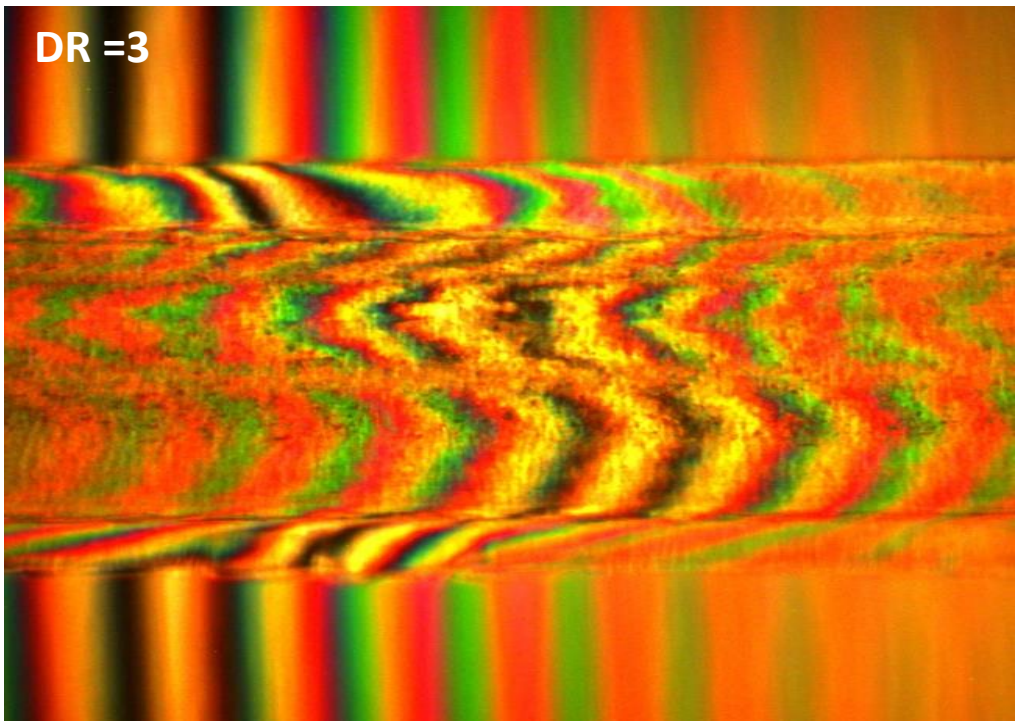

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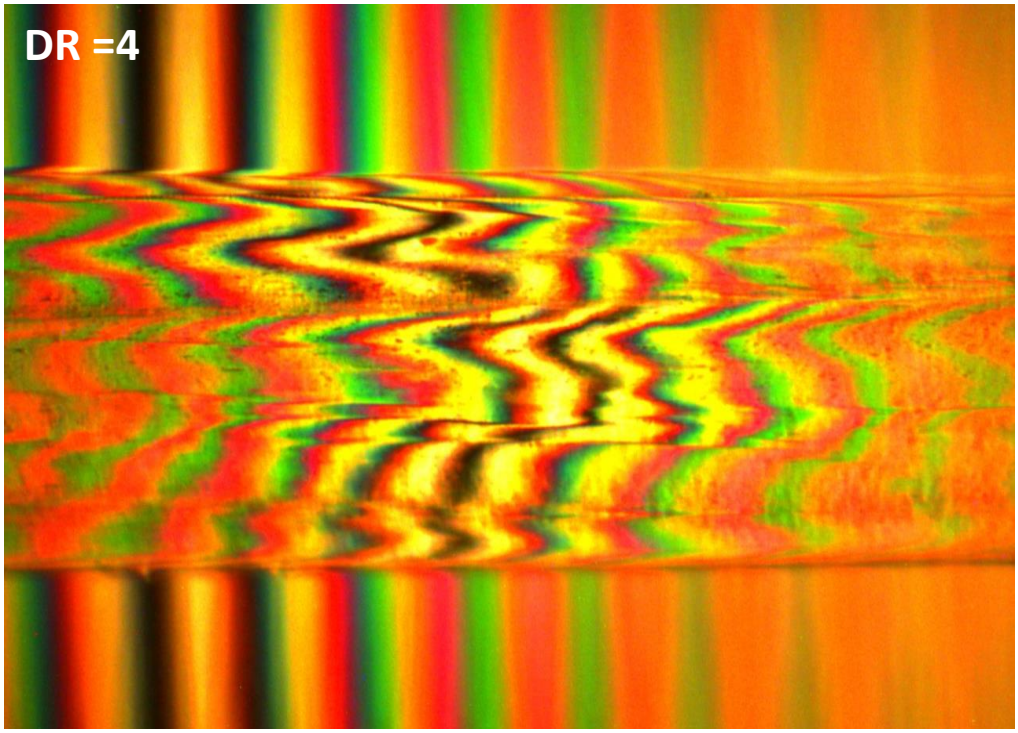

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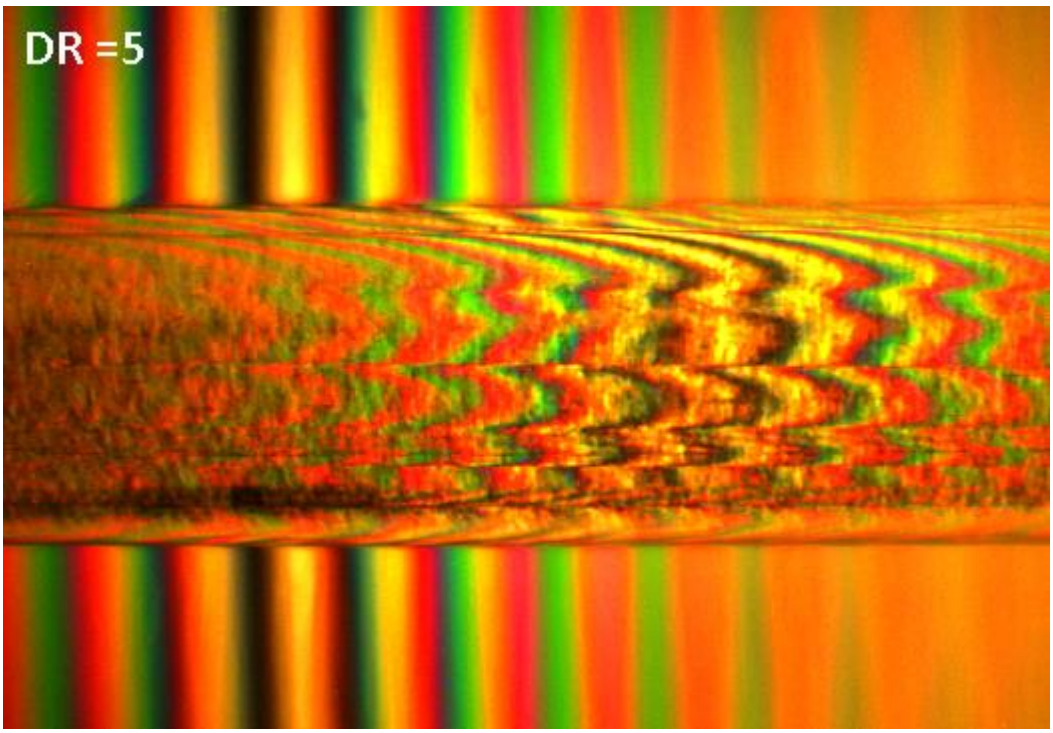

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Figure 4.28 Microinterferograms of Sample C

The microinterferogram of as spun sample C showed slight birefringence as shown in Figure 4.28(a). The improved birefringence was observed in the fibres drawn to 2:1 shown in Figure 4.28(b). The fibres shown in Figure 4.28(c) which was drawn to the 3:1 showed deterioration in the polymer crystal alignment indicated by the reduction in the birefringence. The further deterioration in the alignment were observed when the fibres were drawn to 4:1 the reduced birefringence in indicated in the Figure 4.28(d). While the samples drawn to 5:1 showed improvement in the polymer alignment indicated in Figure 4.28(e).

Draw ratio	Birefringence		
	Sample A	Sample B	Sample C
1	0.00	0.00	0.001 ± 0.001
2	0.007 ± 0.002	0.016 ± 0.003	0.012 ± 0.002
3	0.012 ± 0.002	0.021 ± 0.003	0.010 ± 0.001
4	0.014 ± 0.002	0.026 ± 0.003	0.011 ± 0.002
5	0.015 ± 0.002	0.029 ± 0.004	0.017± 0.003

Table 4.6 Birefringence values of samples at different draw ratio

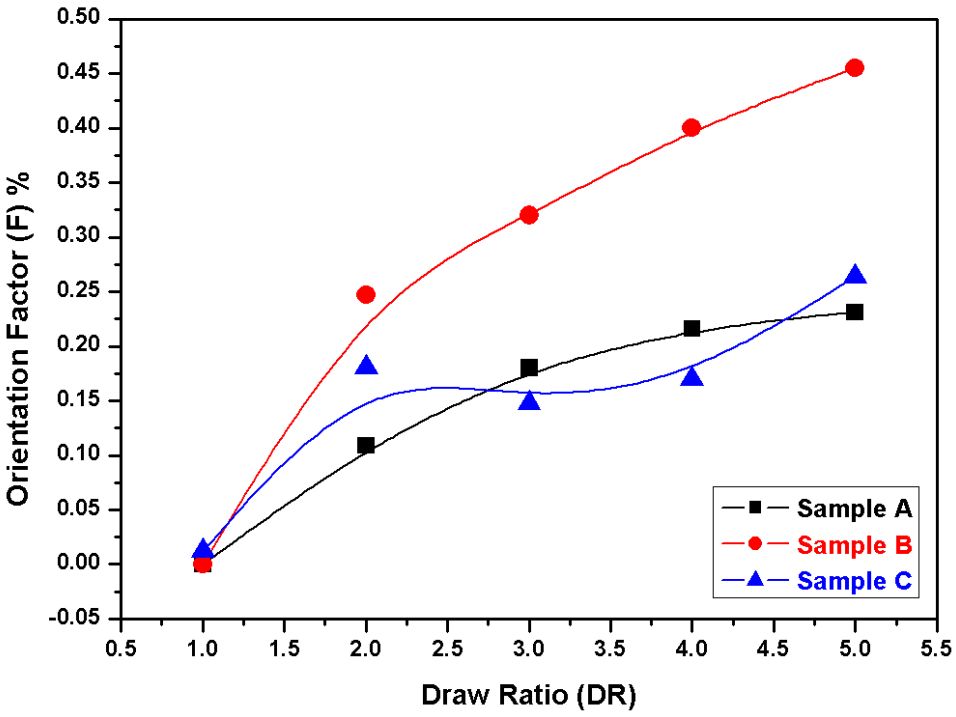


Figure 4.29 Molecular orientation vs. draw ratio

The orientation of fibres treated with the ultrasonic energy was found to be better than the non-treated fibres as shown in the Table 4.6 and in Figure 4.26- Figure 4.28. The graph shown in Figure 4.29 indicates that samples B and C had better

orientation than sample A at a draw ratio of 1 and 2. At draw ratios of 3 and 4, sample C showed less orientation than samples A and B. At the draw ratios of 5, samples C and B showed better orientation than sample A. Sample B showed better orientation than both samples A and C at all draw ratios while sample A only showed a better orientation than sample C at draw ratios of 3 and 4. These clearly indicate the improvement in the orientation of the fibres treated with ultrasonic energy. This improvement in ultrasonic treated fibres was due to the improvement in the arrangement and disentanglement of the polymers during the ultrasonic treatment.

4.8 Summary

A terpene-based process for the spinning of UHMWPE was developed which replaces the hazardous petrochemicals as a spinning solvent. The first objective of the research was to identify a sustainable, environmentally friendly and user friendly solvent for the production of UHMWPE. Since the terpene is a natural solvent from the orange peel, it is sustainable. Due to its biodegradable nature, it does not pose any threat to the environment. Hence the first objective of the research was achieved.

The terpene based process's second feature is the elimination of the secondary solvent which was the second objective of the research. In the case of the petrochemical solvents they needs to be removed by using other more volatile petrochemicals e.g. hexane, cyclohexane etc. Use of these solvents raises more environmental concerns similar to spinning solvent. The solvent removal in the terpene based process is simultaneously takes place during the quenching of the fibres in the water bath. Hence, no extra chemical is required to extract the terpene. This elimination of the secondary solvent eliminates the cost associated with it. It also eliminates the issues of sustainability, environmental and health hazards.

The third objective of the research was the elimination of the extraction stage. The terpene-based process does not require an extra solvent elimination stage hence eliminating the cost associated with the running of the solvent elimination process.

Four factors were investigated for their effects on the strength of the fibres though systematic experimental approach which was the fourth objective of the research. The concentration was found to be the most influential factor followed by the combination of particle size and concentration. The third most important factor was the

combination of concentration and heating time followed by heating time and combination of temperature and concentration.

The fifth objective the research was to investigate the effect of ultrasound treatment for the improvement of the polymer chain alignment. The ultrasound treatment was found to be beneficial in improving the alignment of the fibrils. The samples treated with ultrasonic treatment also showed better strength than the untreated samples.

The strength of the fibres produced by terpene process was found to be weaker than the previously recorded strength. However, in the previously recorded literature the polymer grade used was of lower molecular weight which is easier to extrude. In the present study a higher molecular weight polymer grade was used. Due to this higher molecular weight the polymer chains posses the problem of entanglements which results in the weak places in the fibre. These entanglements were disentangled by utilizing ultrasonic energy. The fibres treated with ultrasonic energy produced fibre with superior strength than the previously reported. The improvement in the strength was due to disentanglement of polymer chains, which resulted in better-oriented fibres.

The first five objectives had been achieved in this chapter. The next chapter addresses the next two objectives related to the development of the coating process.

Chapter 5 **Development of UHMWPE Coating Process**

5.1 Introduction

This chapter presents the research carried out to develop the coating process for UHMWPE to achieve the last two objectives described in the section 1.4. Coating is a widely known process to improve mechanical and physical properties of fabric. UHMWPE has very good chemical and physical properties. Application of UHMWPE coating on to fabrics such as cotton can prove helpful in opening new areas of application for UHMWPE, which were beyond the current possibilities. Cotton fabric was chosen as a substrate due to its availability and comfort properties. Another consideration for choosing the cotton fabric was its poor chemical resistance to acids which was advantageous in testing the coating resistance to acids. There was no literature available regarding the coating of UHWMPE on the fabrics. Unlike other coating materials, the UHMWPE coating was not very straight forward. The problem associated with UHMWPE coating was its very high viscosity and its solutions instability at room temperature. The complete absence of data regarding UHMWPE posed many challenges. Challenges include the preparation of the polymer solutions finding the optimum concentration of the polymer for coating solution, instability of the polymer solution at room temperature as it is well known the polymer solution of UHMWPE undergoes phase separation below a certain temperature. The biggest challenge was to identify the process for the application of the coating onto the fabric. The coating process depends greatly on polymer solution properties. Polymer solution properties such as temperature of dissolution, phase separation temperature, concentration of the polymer etc. are equally important for both gel spinning and coating. The understanding of these properties of polymer solution gained in the gel spinning experiments was useful in developing the coating process. Standard coating processes were investigated for understanding the interaction between fabric and polymer solution during different standard coating processes, this understanding of fabric and polymer solution interaction lead to design a custom made coating machine for the coating of the UHMWPE.

5.2 Initial Coating Experiment

Dip coating was chosen for the initial experiments to coat the fabric, as the dip coating does not require any special equipment and depends on the viscosity of the

coating solution. It was understood that the viscosity of the UHMWPE solution differed greatly depending on the solvent in which polymer is dissolved. The concentration was the other main factor which influenced the viscosity of the polymer solution. Viscosity was not only dependent on the concentration of the polymer in the solution but also on different solvents which provided different viscosities at the same concentrations. It was decided to experiment with different solvents separately to find the solvent which was most advantageous for the process.

5.2.1 Paraffin as Solvent

Paraffin oil was one of the easier solvents to work with as it had a high boiling point. The coating solutions were prepared by heating 1% and 5% at 150^{o}C for 24 hour. 1% (w/v) 2,4-Dimethyl-6-tert-buthylphenol was added in the solutions to avoid oxidation of the polymer. Fabric samples of cotton were dip coated in the hot solution at 150^{o}C. It was observed that the 5% solution was too viscous; consequently, no coating was achieved while the 1% solution was able to coat the fabrics although the coating was not uniform due to the sticky nature of the coating solution. The other problem paraffin based coating presented was the removal of the paraffin oil from the coated fabric. Due to the high boiling point of the paraffin oil it could not be removed by drying. It was found that the paraffin could not be removed without using a removal solvent, which also resulted in removal of the coating.

5.2.2 Decalin as Solvent

The problem in removing the paraffin oil resulted in the selection of a solvent, which has lower boiling point so the solvent could be removed easily without damaging the coating. Decalin was chosen due to its lower boiling point. The coating solutions were prepared by heating 1% and 5% solutions of UHMWPE in Decalin at 150^{o}C for 40 min under nitrogen. The fabric samples of cotton and polyester were dip coated in the hot solution. The coated samples were dried by leaving in ambient conditions overnight then by vacuum drying for 24hr. The coated samples were found to be coated well but very uneven.

5.2.3 Kerosene as Solvent

The coating solutions from kerosene were prepared by heating 1% and 5% solutions of UHMWPE at 135^{o}C for 45 min. The samples of cotton fabrics were dip

coated in the hot solution. The samples were dried by putting in the oven at 100^{o}C for 30 min.

5.2.4 Terpene as Solvent

The coating solutions were prepared by dissolving 1% and 5% UHMWPE in terpene at 130^{o}C for 45 min. the coating was applied on the samples of cotton and polyester fabric by dip coating method. The samples were dried in an oven at 100^{o}C for 30 min.

5.2.5 Concentration of Gel

The coated samples showed that the uniformity of the coating increased with lower concentration; the samples coated with 5% solutions were less uniform than the samples coated with 1% solution though the solvents used did not influence the coating uniformity except paraffin samples. In the paraffin samples, it was found to be difficult to remove the paraffin oil without damaging the coating. The paraffin was therefore eliminated as a solvent for further experiments.

5.2.6 Dip Coating

The uniformity of the dip coating depended on the viscosity of the coating solution. The coating solution of the UHMWPE in all solvents behaved as a sticky gel thus the uniformity of the coating achieved was poor. Even at very low concentrations i.e. 0.3% the coating solution behaved as a sticky gel. Due to this nature of the coating solution, it was decided to investigate an alternative coating method.

5.2.7 Coating with Rod on Table

To control the thickness and improve the uniformity of the coating, the 'Wire wound rod' coating process was adopted (Figure 5.1). Initially wire rods were used to coat the fabric but due to very sticky nature of the coating solution, the movement of the solution was not uniform resulting in non-uniform coatings. The wires on the wire rods increased the unevenness by providing more points where solution can stick.

Figure 5.1 Wire wound coating rod

Figure 5.2 Wire wound coating rod groves

The wire rod was replaced with a plain rod, which presented a secondary problem. In the wire rod, the thickness of the wire groves indicated in Figure 5.2

provided the uniform clearance between the table and the rod hence controlled the thickness of the coating while in the case of the plain rod this clearance was not possible. To overcome this problem, special collars were placed on the two opposite sides of the card. The height of the collars determined the clearance between the card and the rod schematic is shown in Figure 5.3. To coat the fabric the samples were placed on the card. With the collars on the two opposite sides, the solution was poured over the fabric and the rod used to spread the solution evenly. The excess solution was allowed to flow out from the both top and bottom openings. This coating method presented its own problems. The coating solution showed phase separation when cooled down lower than its phase separation temperature (the fabric samples coated were at ambient temperature). When the coating solution was poured onto fabric, the solution cooled and phase separation occurred. As there was no external heat source in the setup. The solution could not be maintained above the phase separation temperature; hence, the coating of the fabric could not be applied satisfactorily.

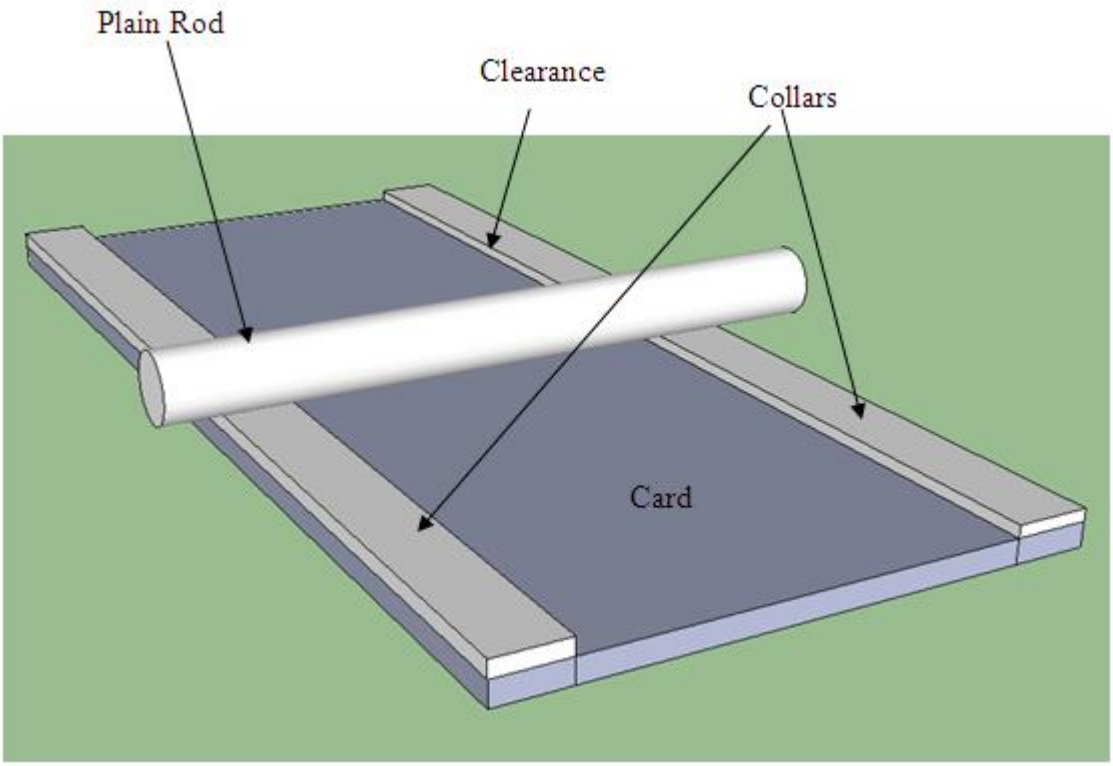


Figure 5.3 Coating card with collars to provide clearance

5.3 Modification of the Coating Machine

Coatings were also applied using a Coatema Basecoater BC 06. The machine worked on the knife on roller principle discussed previously in detail in Chapter 3. The initial trials on the machine resulted in uncoated to poorly coated samples. The reason was similar to the wire-rod experiments i.e., the coating solution cools down as it is exposed to the fabric at room temperature. In the case of the Coatema Basecoater BC 06 the knife itself assists in reducing the solution temperature, which causes the phase separation in the solution hence, resulting in a poor coating. In order to overcome the phase separation during the coating process, there was a need to maintain the solution above its phase separation temperature to achieve coating.

Modifications in the machine were needed to keep the solution above the phase separation temperature. The modified parts should be interchangeable with the original part so the machine could be used with its original parts if needed. As shown in Figure 5.4 the knife assembly consisted of knife, paste basin and coating roller. The paste basin was the part where the solution is exposed to the fabric and where the reduction in the temperature of the solution occurs so it could have been ideal to place a heater somewhere in the basin to heat the solution. However, because the basin was made of Teflon which is not very good conductor of heat and cannot resist very high temperatures it was not practical to attach a heater in the paste basin. The alternative was to heat the knife since this was the last point where the coating solution encounters the knife assembly. It was decided the modification would be made to heat the knife. It was observed the knife was in contact with the two holding arms that were attached to two pneumatic assemblies.

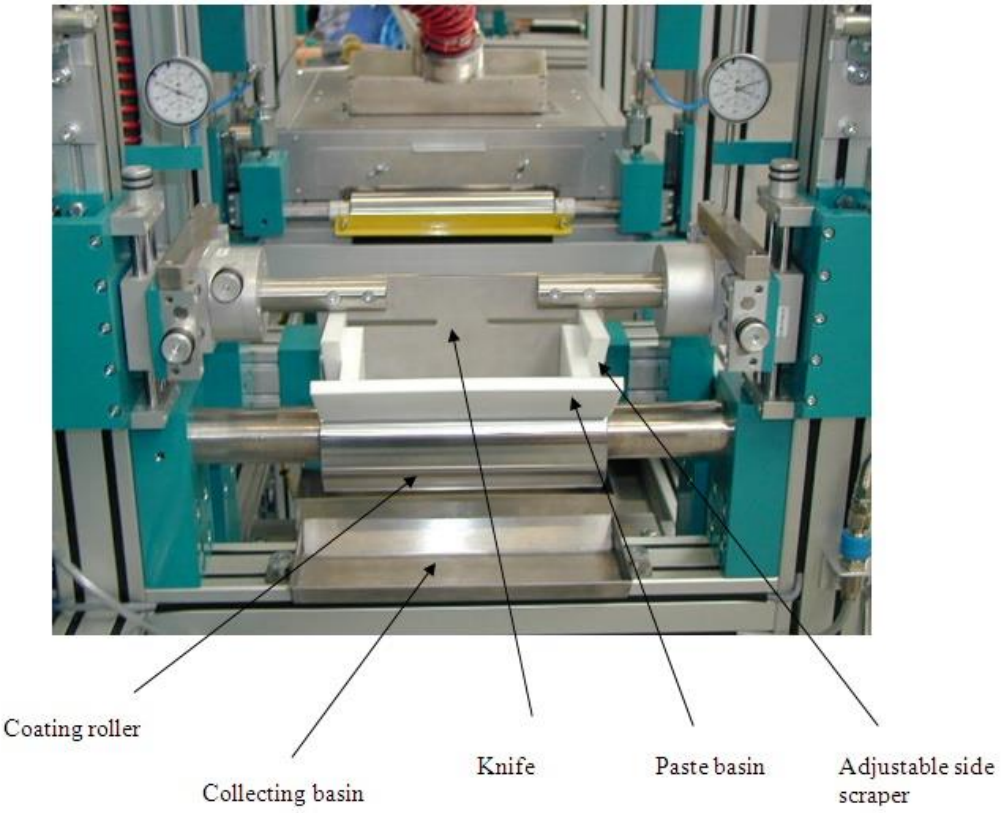


Figure 5.4 Knife Assembly of Coatema Basecoater BC 06

As these contact points were all metallic they were good conductors of heat and if the knife was heated these contact points would cause the transfer of heat resulting in heating the whole machine, which could damage the other parts of the machine. A new knife was designed with Teflon sheets between the knife and the holding arms. The new design thermally isolated the knife from the machine. The new knife was designed to allow the placement of the Teflon sheets. The original knife was 5 mm thick and was tightly fitted in the arm slit gap. To allow the placement of the Teflon sheets, the thickness of the new knife was reduced from 5 mm to 3 mm as indicated in Figure 5.5. The 2 mm clearance was made to allow the placement of a 1 mm thick Teflon sheet on each side.

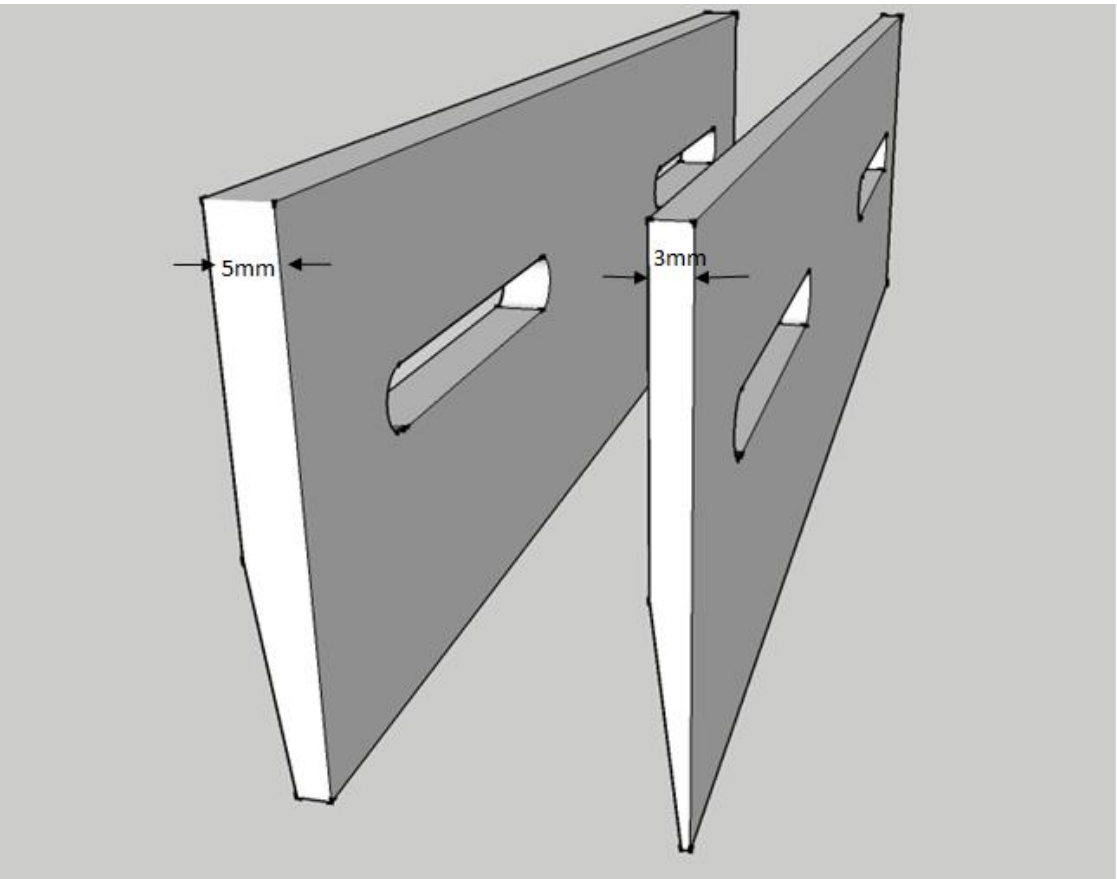


Figure 5.5 Original and modified knife

The second important challenge was to find the appropriate heating mechanism which would not interfere with the coating process and at the same time maintain the temperature of the coating solution. Flexible silicon rubber fibreglass insulated self-adhesive rectangular heaters were selected to heat the knife. They provided the advantage of being attached to the lower backside of the knife providing the heat directly to the area where the solution was going to be in contact with the fabric Figure 5.6 shows the heater attached to the back side of the knife. The second advantage of placing the heater in the manner described above was that the heaters were not in direct contact with the solution hence avoiding the complications related to insulation.

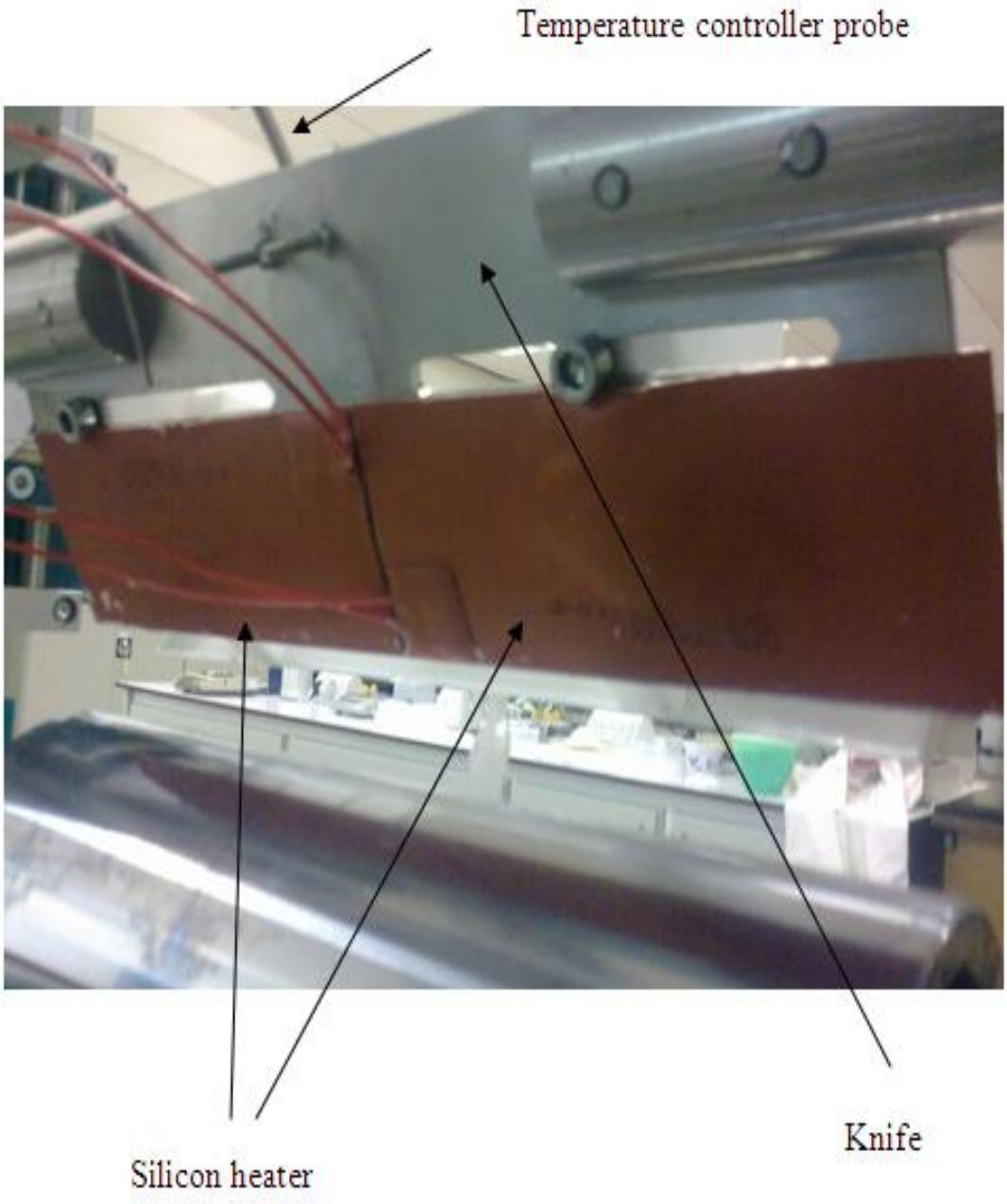


Figure 5.6 Heater attached to the lower part of the knife

The heaters in the size required were only available in 110 volt ratings. Two heaters of 13×5 cm with 110 volts ratings were connected in series as circuit shows in Figure 5.7 to use them on a 220 volt power supply due to the unavailability of a heater which can work at 220 volts standard UK power supply.

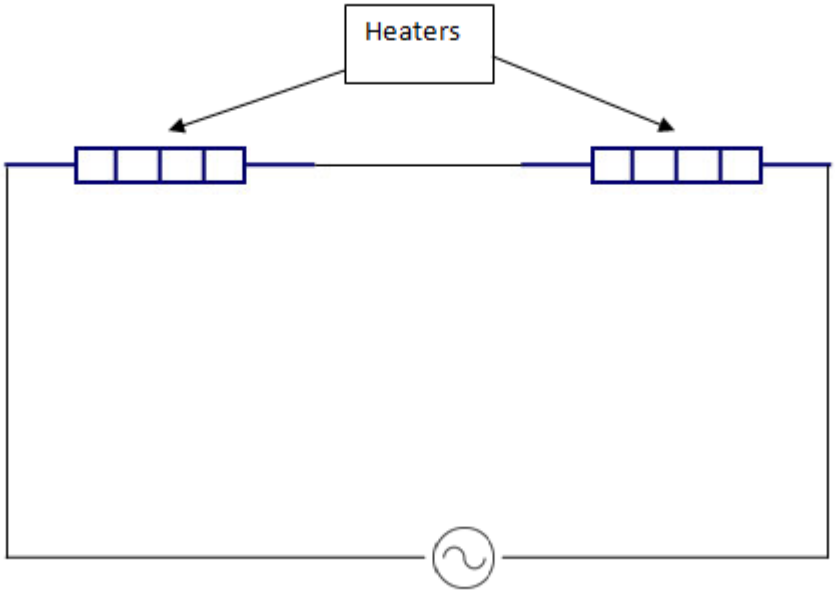


Figure 5.7 Heaters connection circuit diagram

To control the temperature of the heater a temperature controller was used. The sensing probe of the temperature controller was attached to the knife with the help of a metal clamp as shown in Figure 5.8.

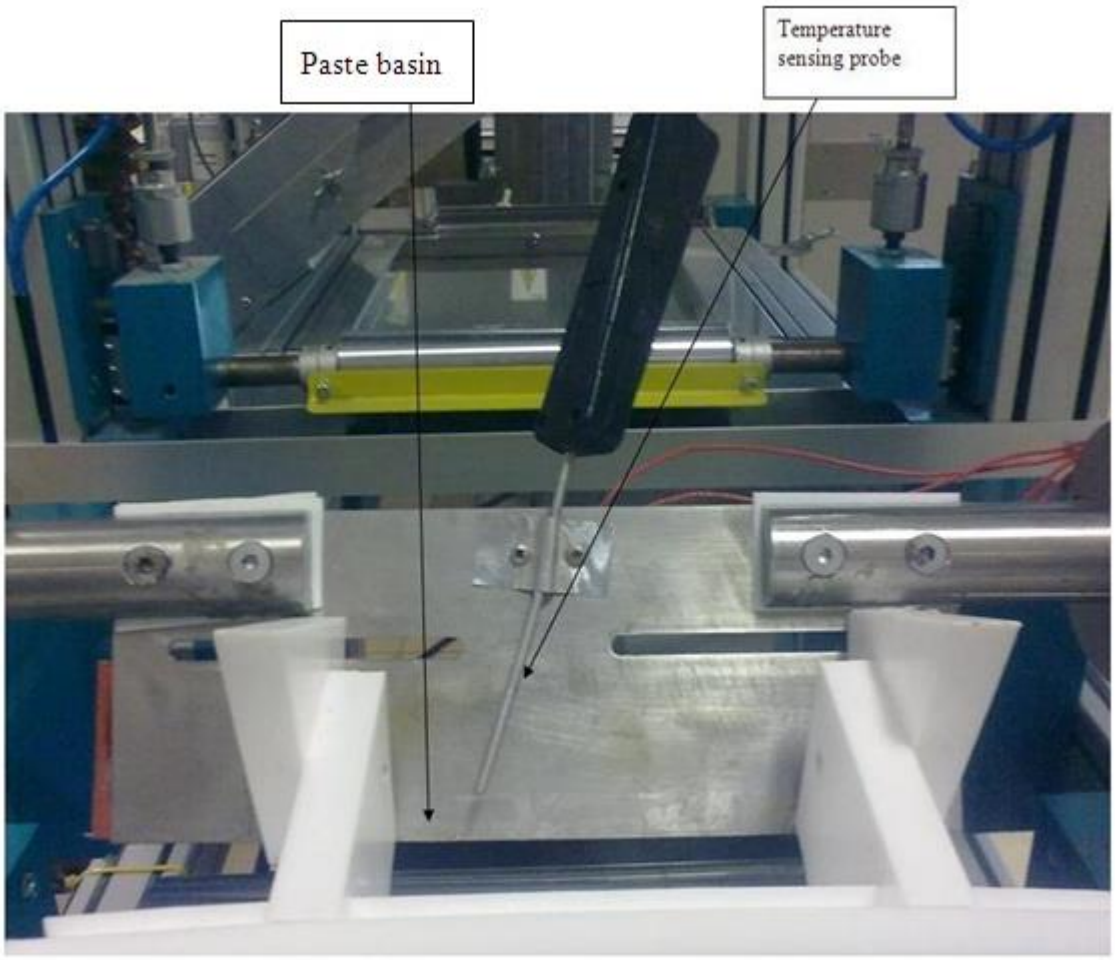
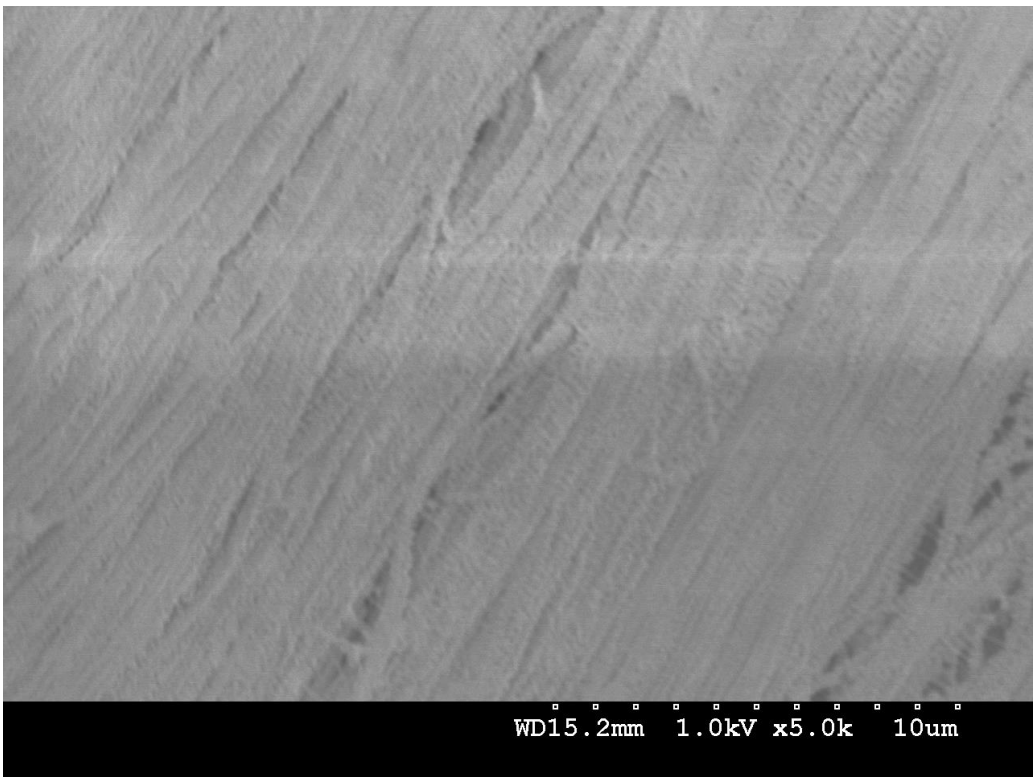


Figure 5.8 Temperature sensing probe placement on the knife

The heaters were attached to the temperature controller to control the temperature of the coating solution by switching the heaters on and off.

5.3.1 Coating with the Modified Coating Machine

Cotton fabric samples were coated on the modified coating machine with a 1% UHMWPE polymer solution. The fabric samples used for the coating were 0.632 mm thick. To control the thickness of the coating the clearance between the blade and the roller was set with the help of leaf gauge. Two different thicknesses of the coating were applied on the fabric (0.1 mm and 0.6 mm). The temperature of the blade was set at 120^{o}C and the temperature of the dryer was set at 60^{o}C. The samples were left to dry in ambient conditions over night. The SEM images of the coated samples were taken (Figure 5.9 a-f and Figure 5.10 a-e).



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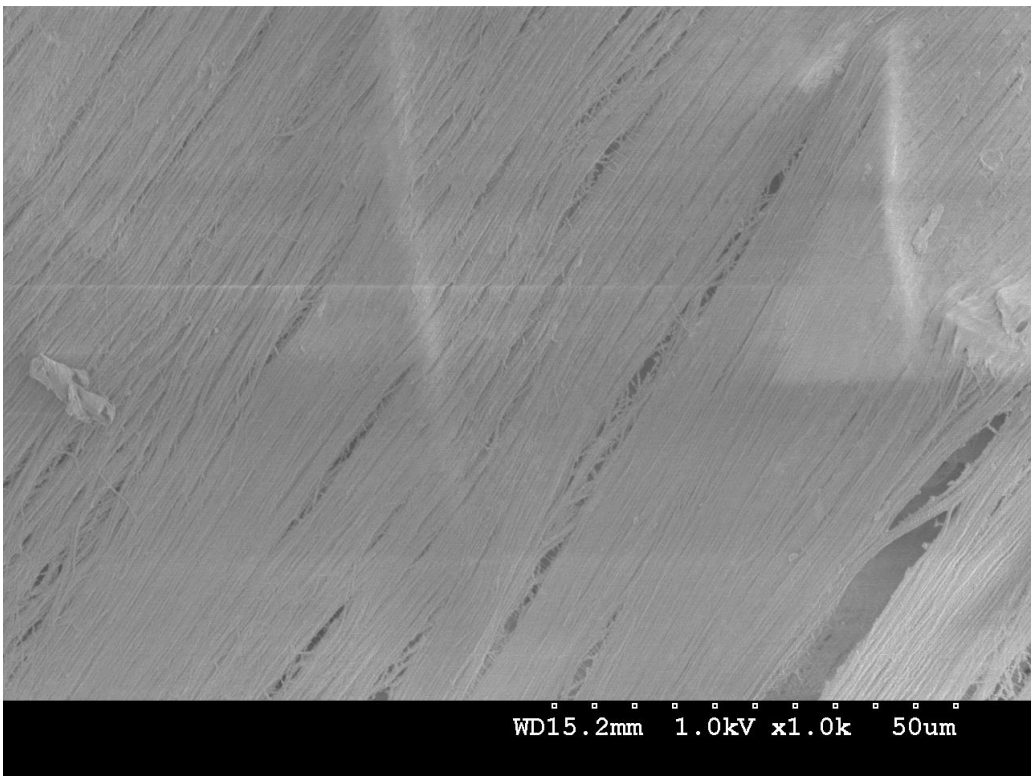

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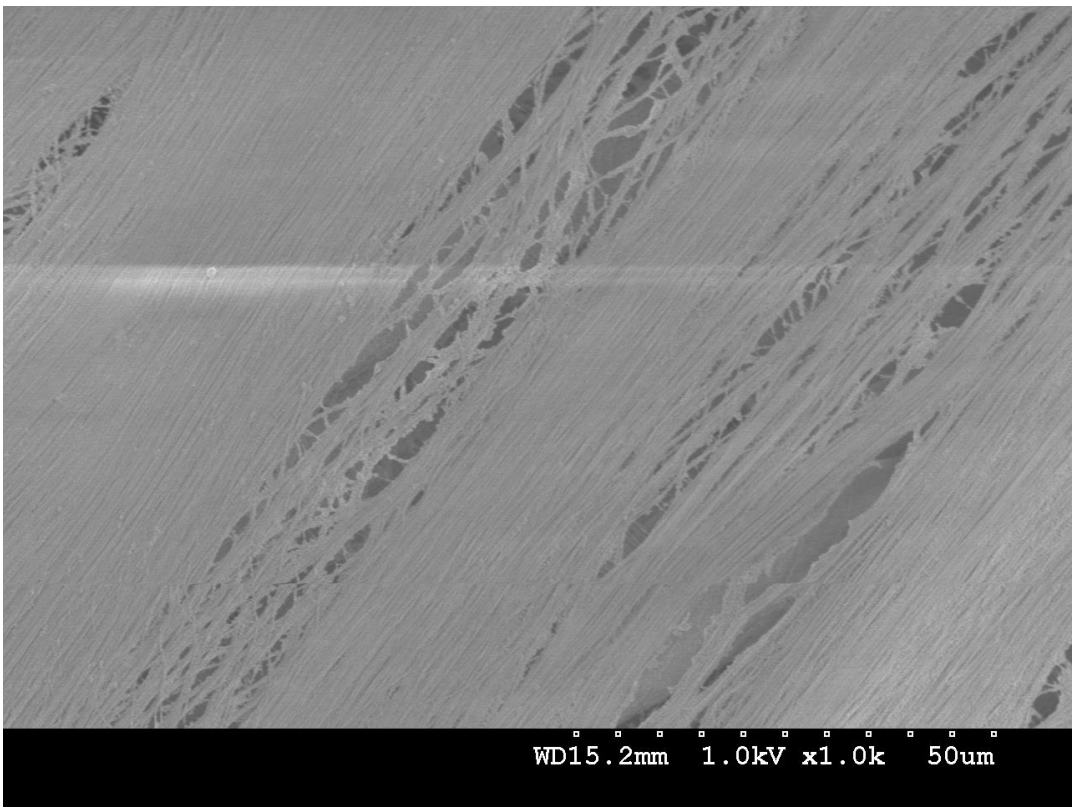

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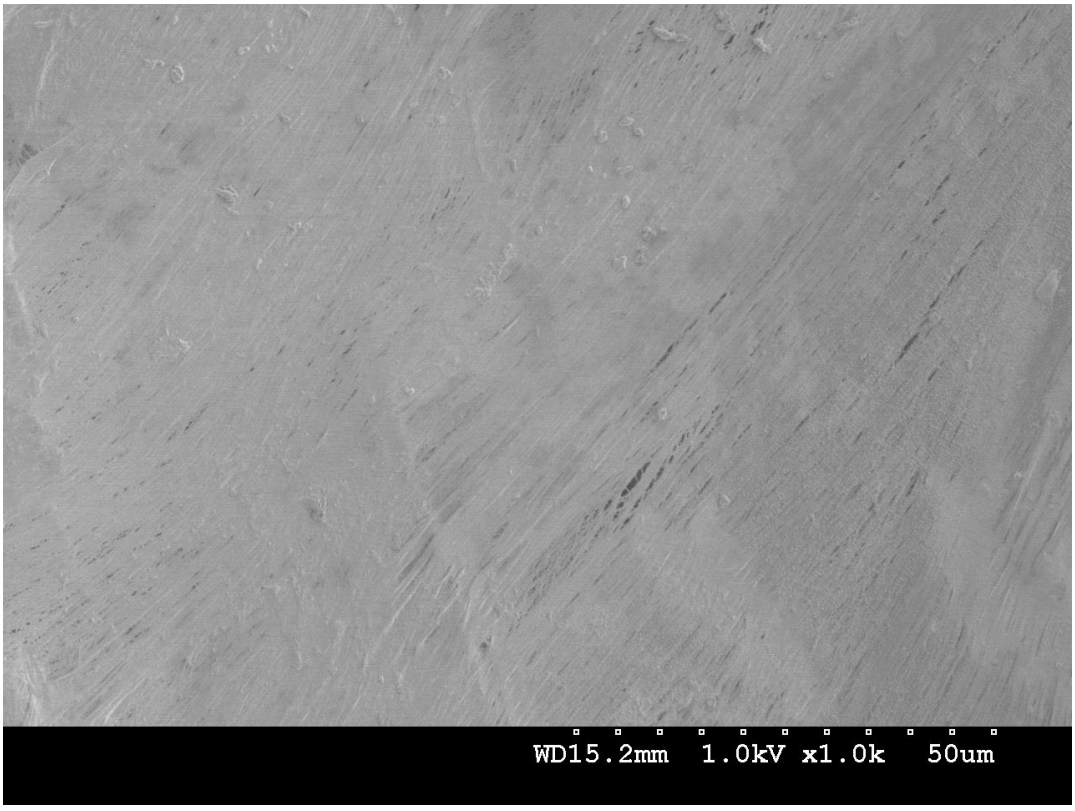

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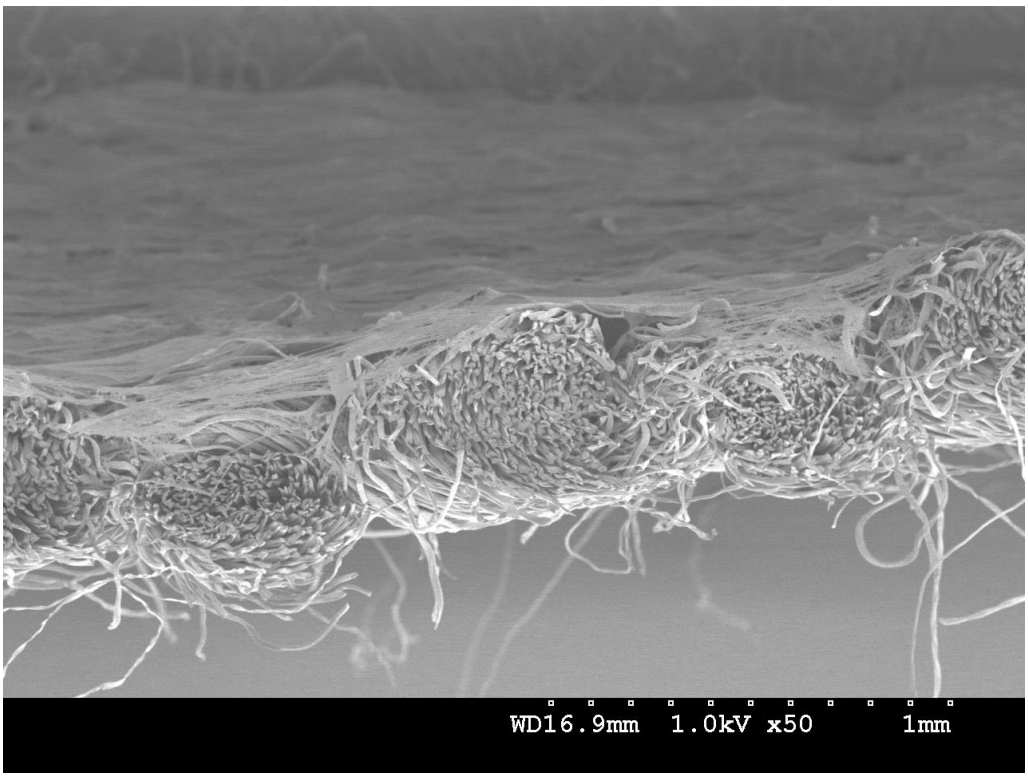

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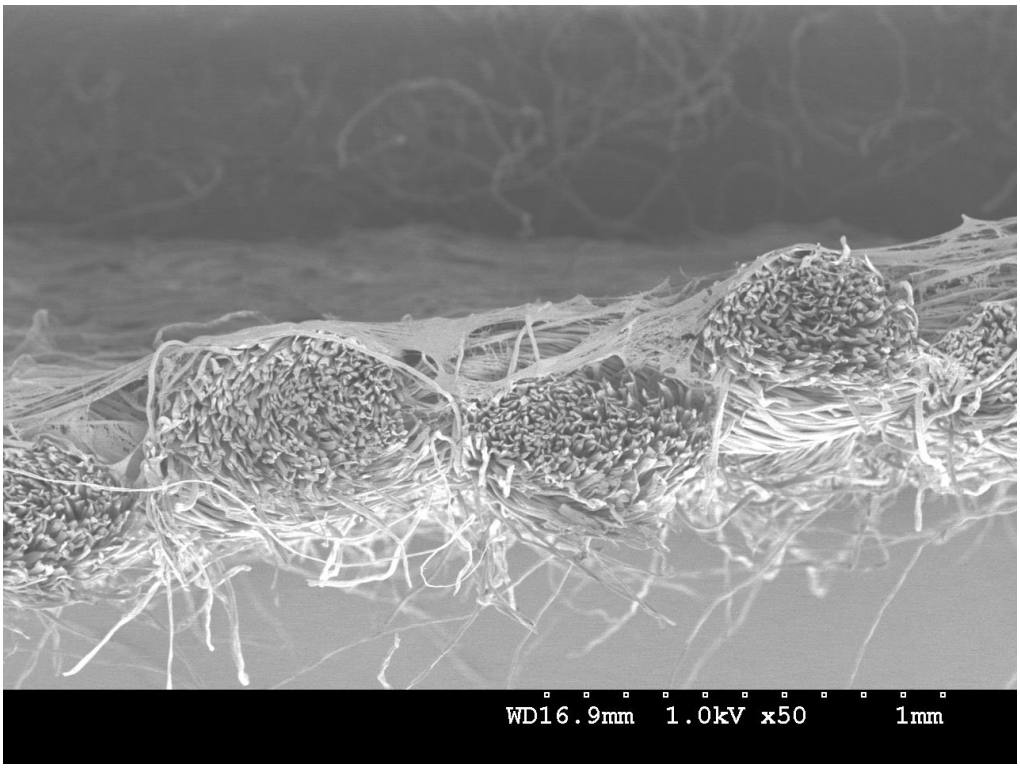
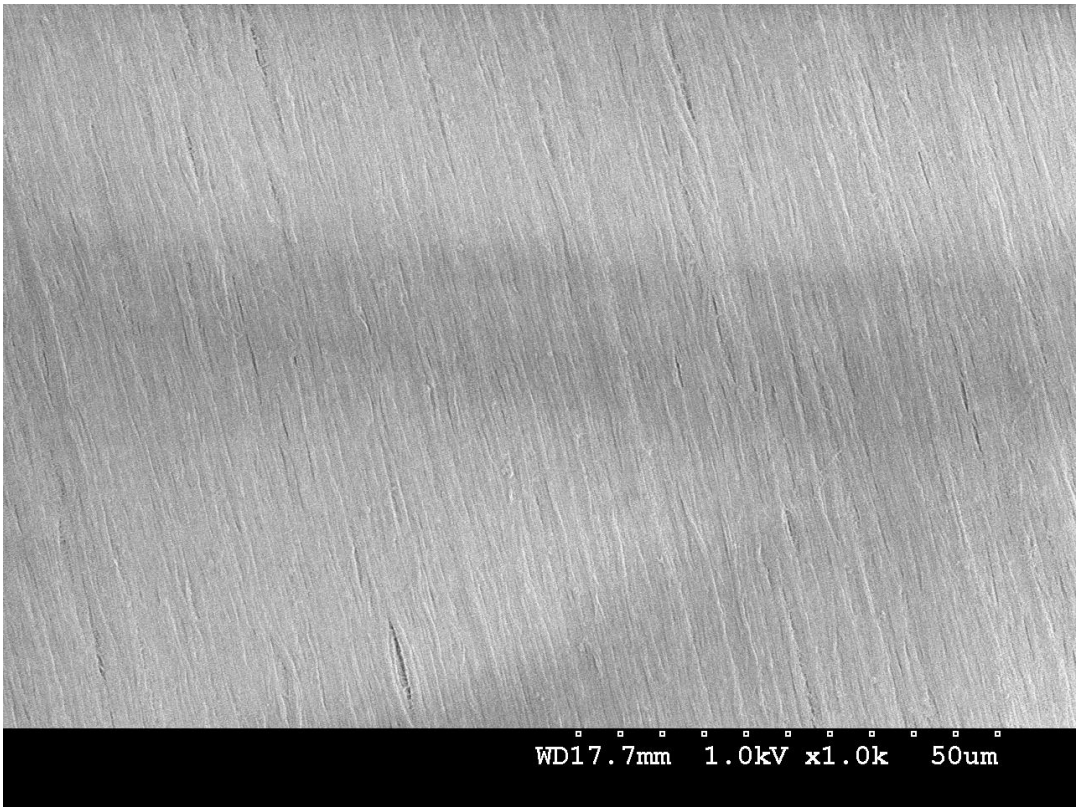


f

Figure 5.9 SEM images of fabric coated with 0.1 mm thick coating

Figure 5.9 (a) shows a SEM image of the 0.1 mm thick coated fabric magnified to 5000 times small cracks were visible in the image. The image shown in Figure 5.9(b)

was magnified to 1000 times this image also showed the cracks in the coating. Figure 5.9(c) which was also magnified to 1000 times showed bigger cracks than the Figure 5.9(b). Significant reduction in the cracks was observed in the Figure 5.9(d). The cross section SEM images of the coating shown in Figure 5.9(e and f) showed the coating is too thin and irregular.



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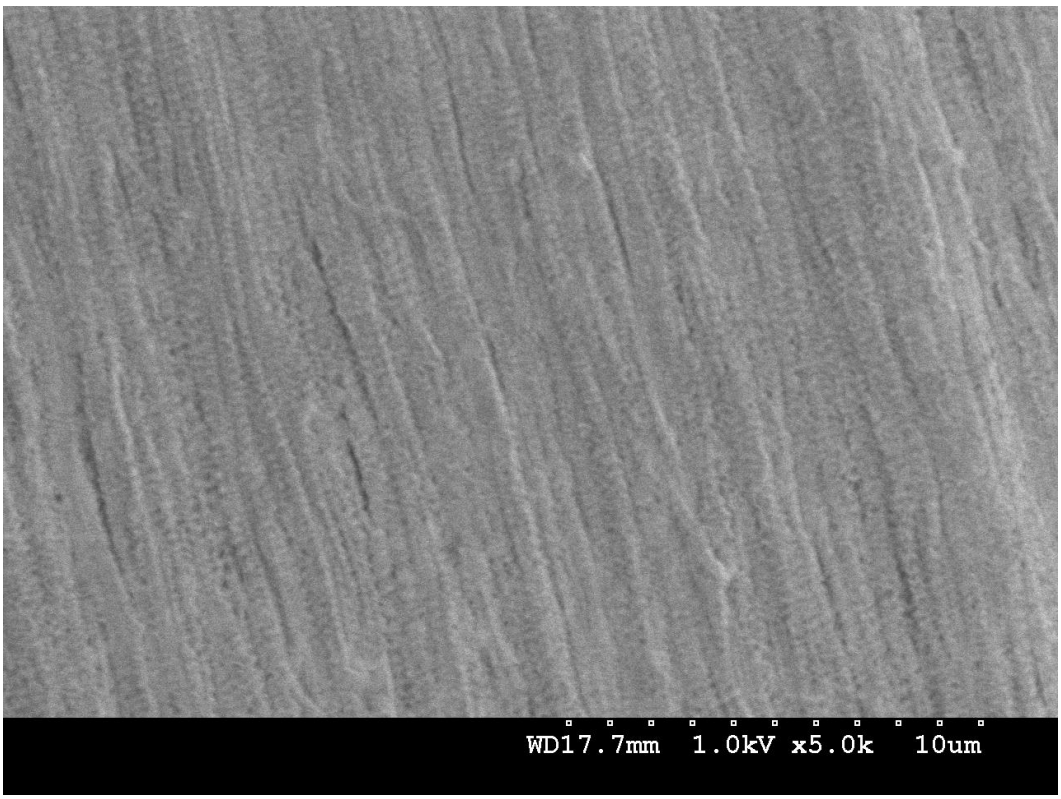

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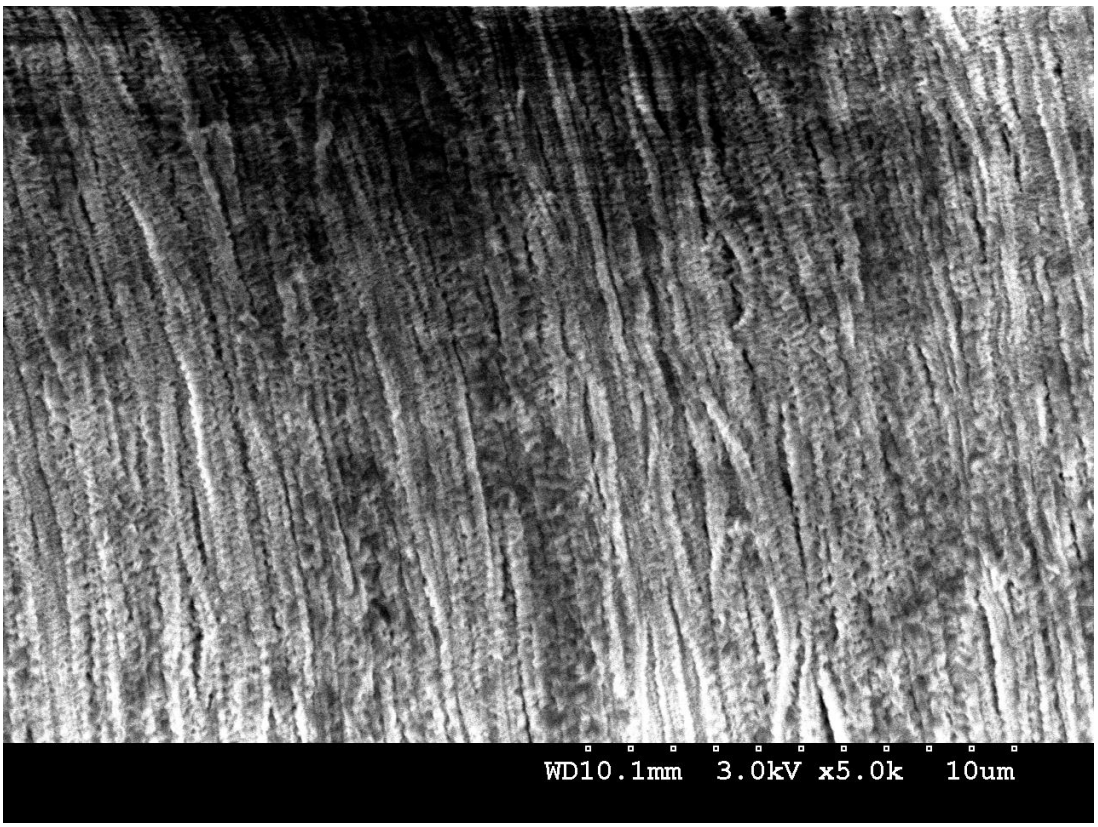

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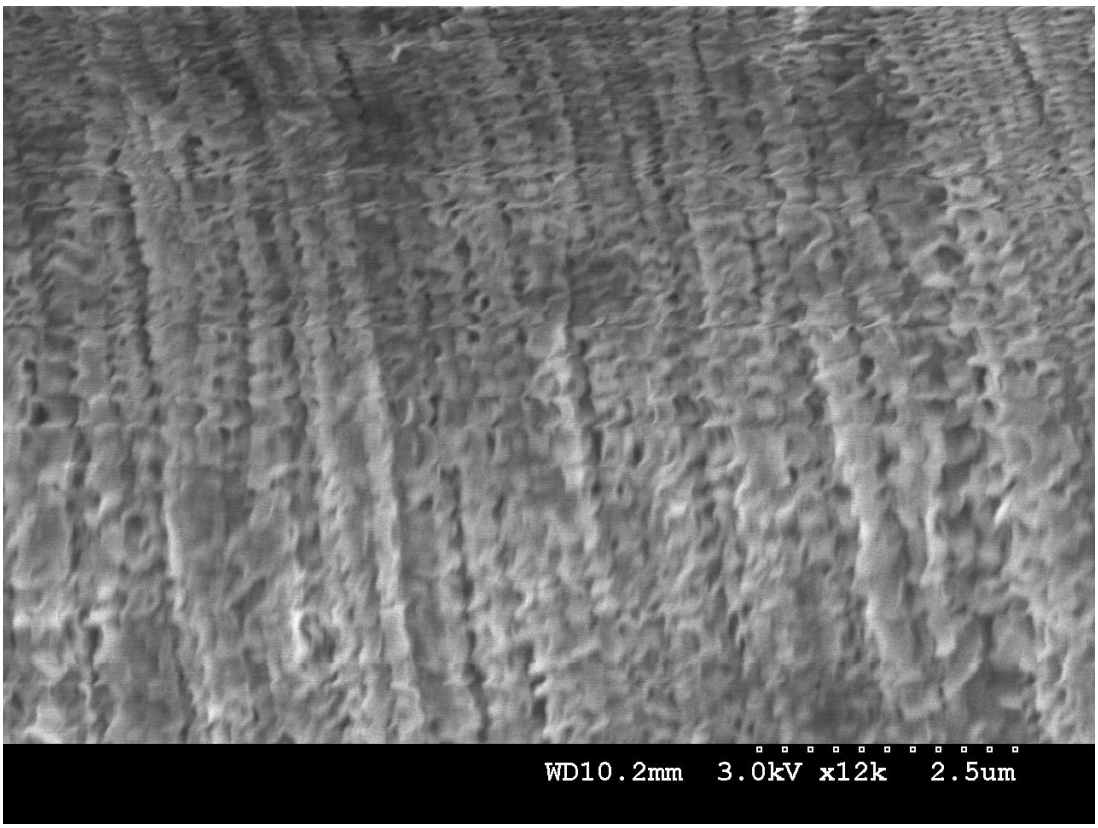


d

e

Figure 5.10 SEM images of fabric coated with 0.6 mm thick coating

The SEM images of 0.6 mm thick coating magnified to 1000 times shown in Figure 5.10(a) shows a uniform coating surface. The images of 0.6 mm coating when magnified to 5000 times as shown in Figure 5.9(b) shown very uniform coating layer with no cracks. The other sample magnified to the same magnification also showed the same uniform coating layer indicated in Figure 5.9(c). Even at 12000 magnification the coating layer appears to be uniform as shown in Figure 5.9(d). The cross section SEM image of the 0.6 mm thick coating is shown in Figure 5.9(e). The images indicates the application of 0.6 mm thick coating result in a 38.3 micron thick coating layer after the removal of the solvent.

The SEM images of the samples with 0.1 mm thick coating shown in Figure 5.9(a-f) indicates presence of many cracks. The cross sectional images of the samples showed a thin irregular coating while the samples coated with 0.6 mm thick coating shown in Figure 5.10(a-e) had uniform coating. The cross section of the samples showed a coating thickness of 38.30 µm.

5.3.2 Chemical Resistance of Coatings to Acids

The sample with the 0.6 mm thick coating was tested for resistance against acids i.e. nitric acid and sulphuric acid. Only samples of 0.6 mm thick-coated samples were chosen due to the significantly less coating defects in comparison to the 0.1 mm thick-coated samples. The coated samples and the plain fabric samples were exposed to acids by placing a drop of acid on both fabrics at the same time. The coated fabric was visually inspected against the plain fabric at 10 min intervals for half an hour.

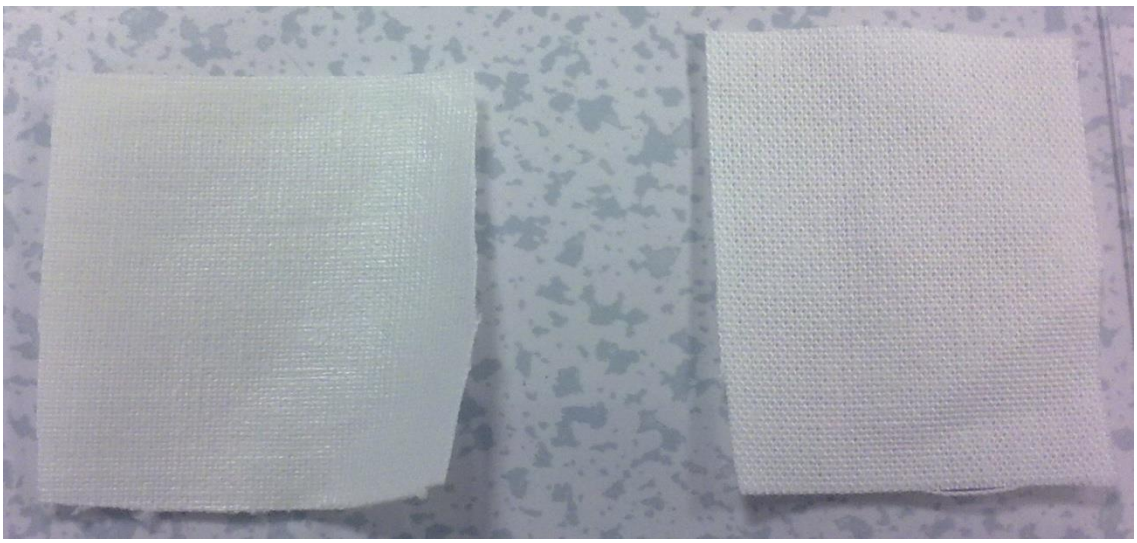


Figure 5.11 Coated sample (on left side) and uncoated sample (on right side)

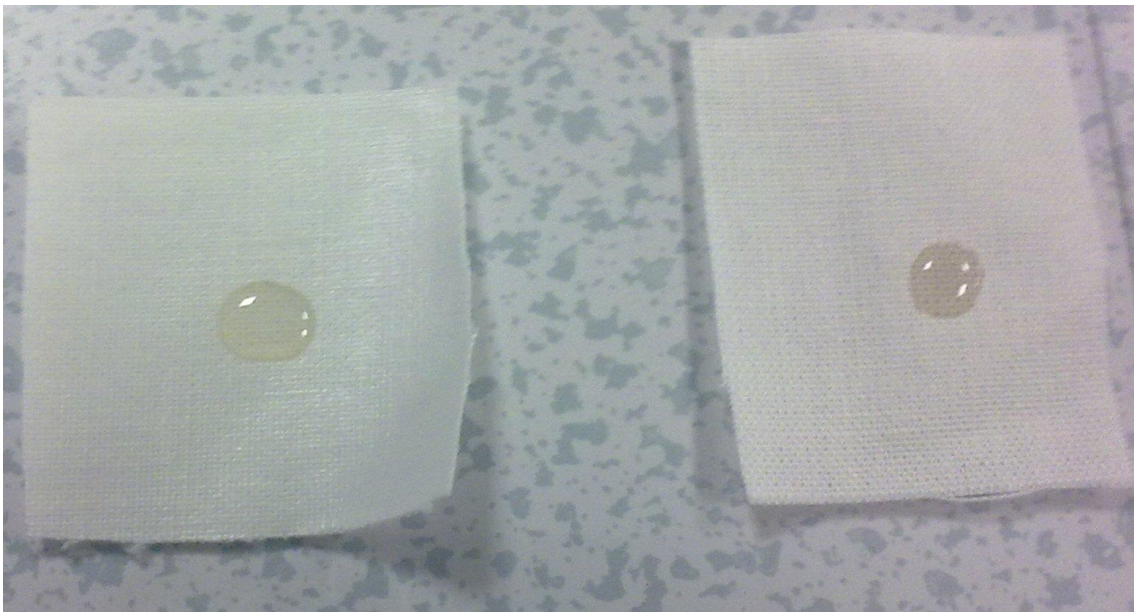


Figure 5.12 Sulphuric acid placed on the coated and uncoated samples

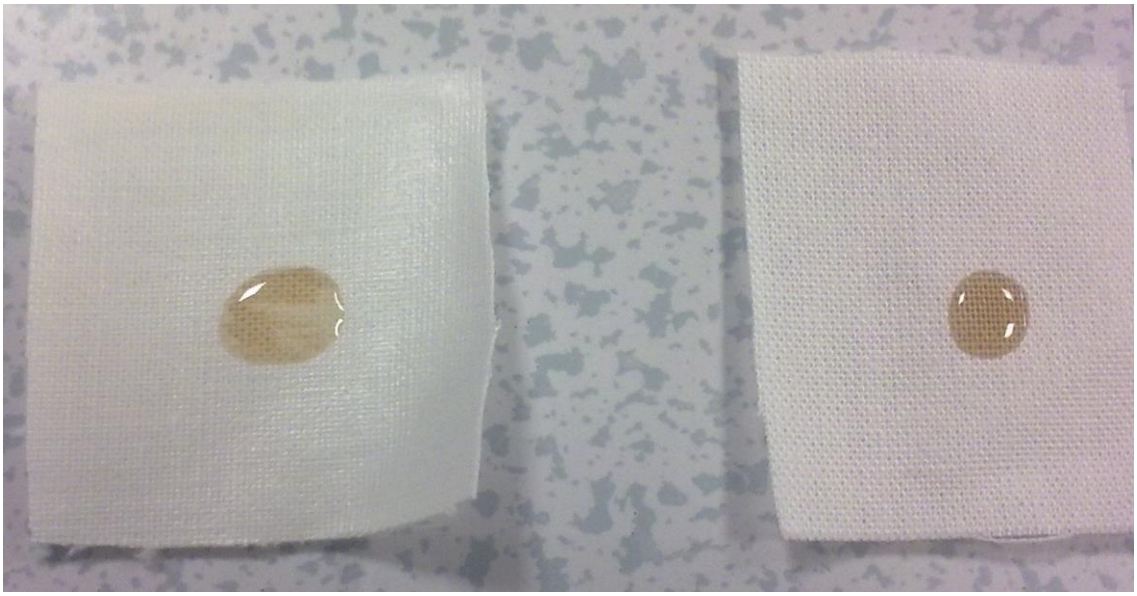


Figure 5.13 Samples after 10 min

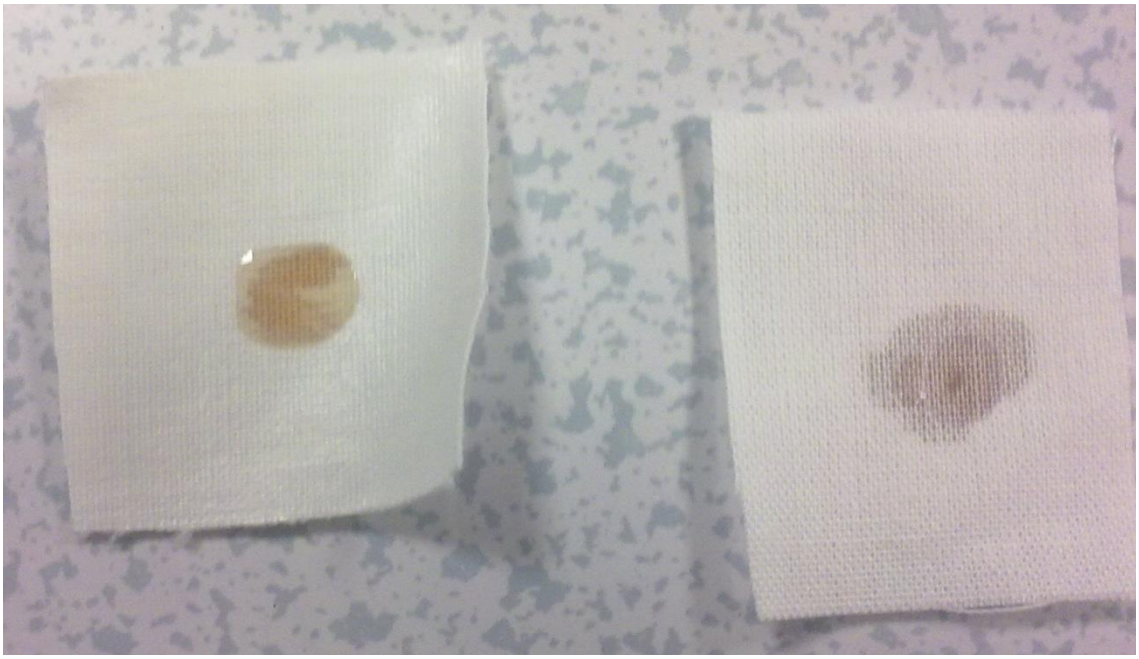


Figure 5.14 Samples after 20 min

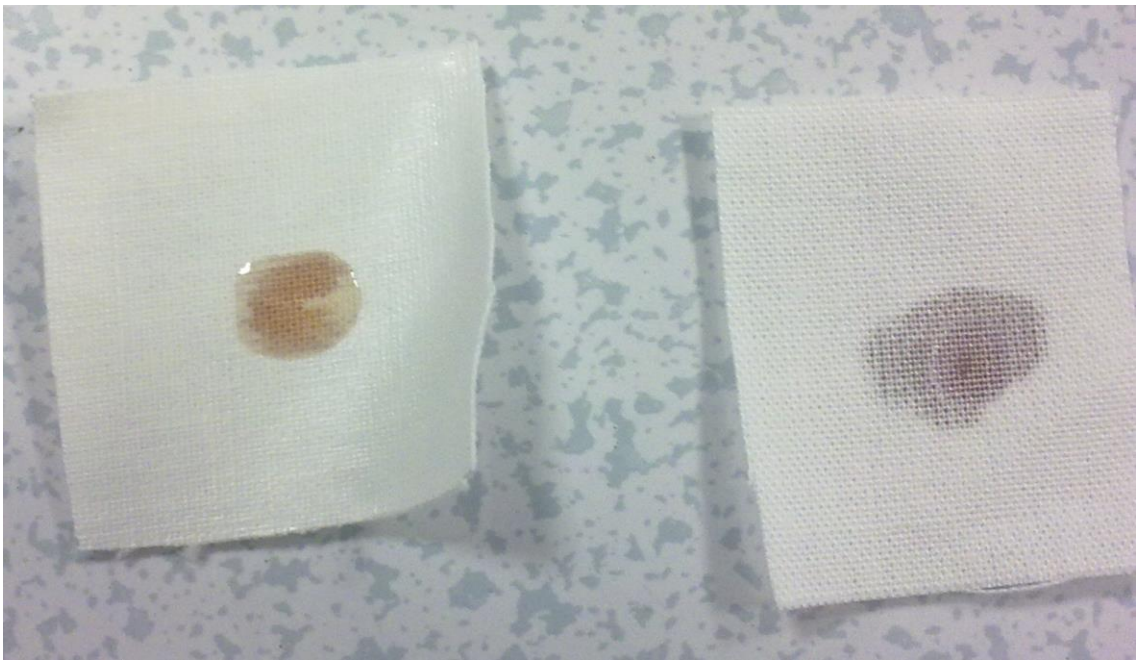


Figure 5.15 Samples after 30 min

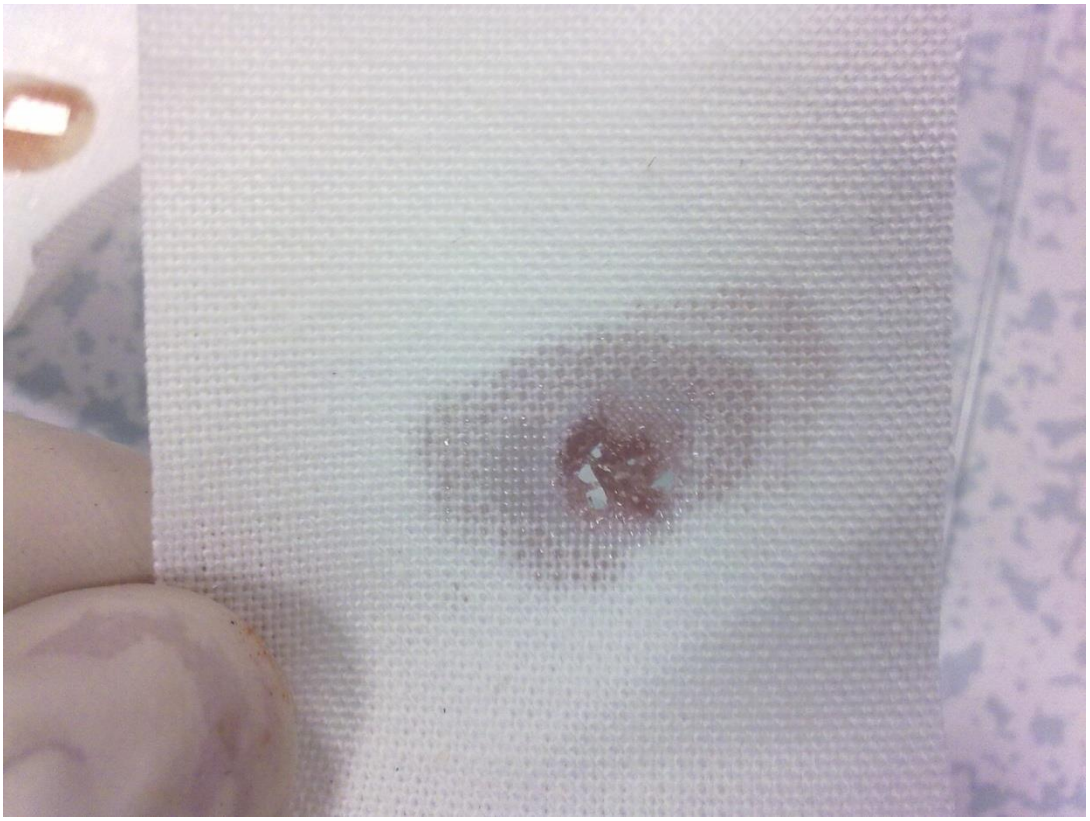


Figure 5.16 Uncoated sample after 30 min exposure to sulphuric acid

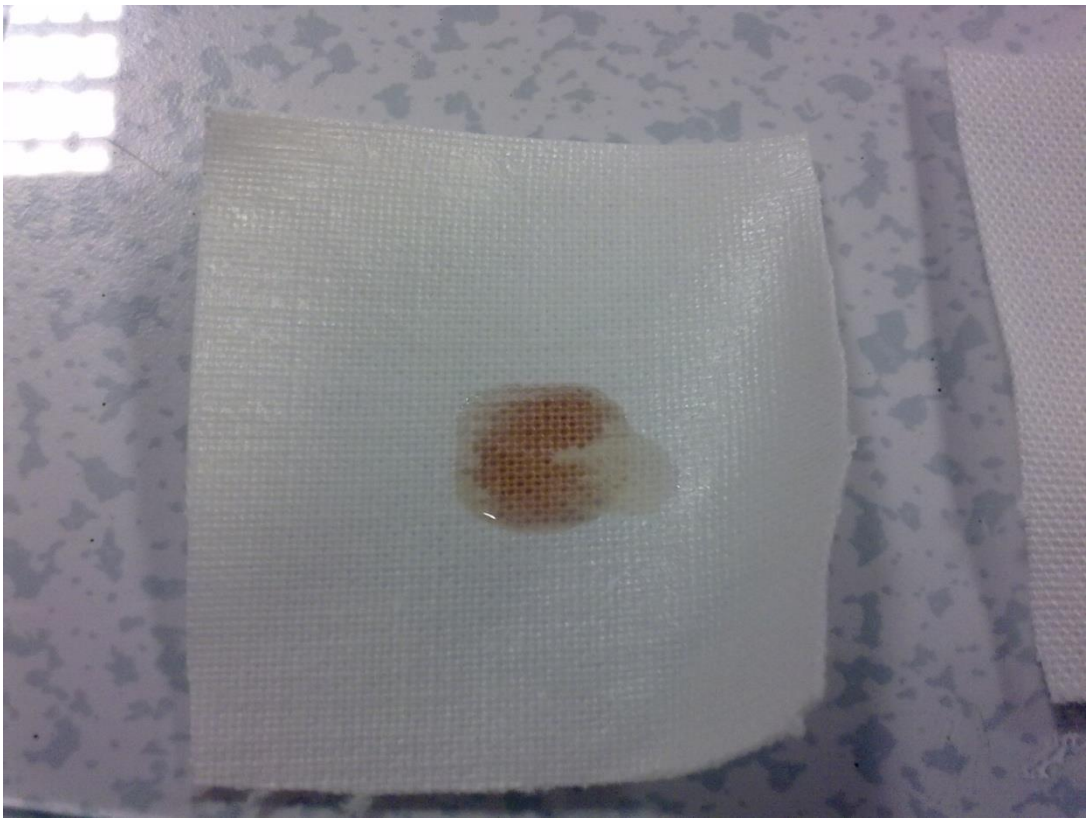


Figure 5.17 Coated sample after 30 min exposure to sulphuric acid

The coated sample exposed to the sulphuric acid showed better resistance than the plain fabric. After 10 min, the plain fabric sample absorbed the sulphuric acid and

started to degrade while the acid did not penetrate the coated sample (Figure 5.13). At 20 min interval, there was slight seepage of sulphuric acid through the coated fabric (Figure 5.14). After 30 min, a significant amount of sulphuric acid had seeped through the coated samples. The plain fabric on the other hand had completely decomposed (Figure 5.14-Figure 5.17) while in the case of the coated sample, there was seepage of acid but the coating did not become damaged.

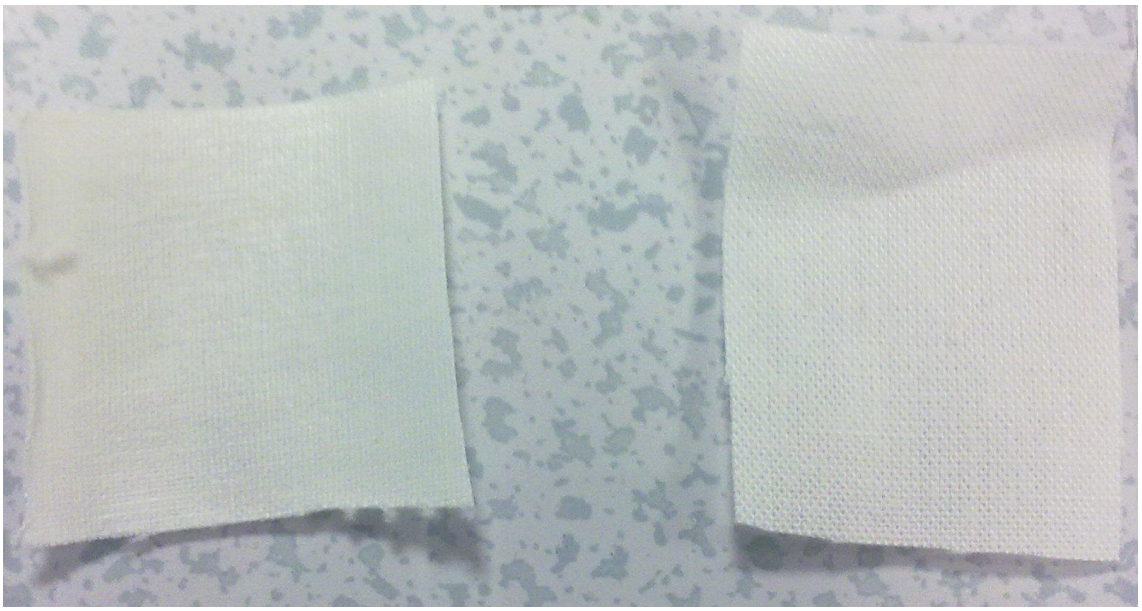


Figure 5.18 Coated sample (on left) and uncoated sample (on right)

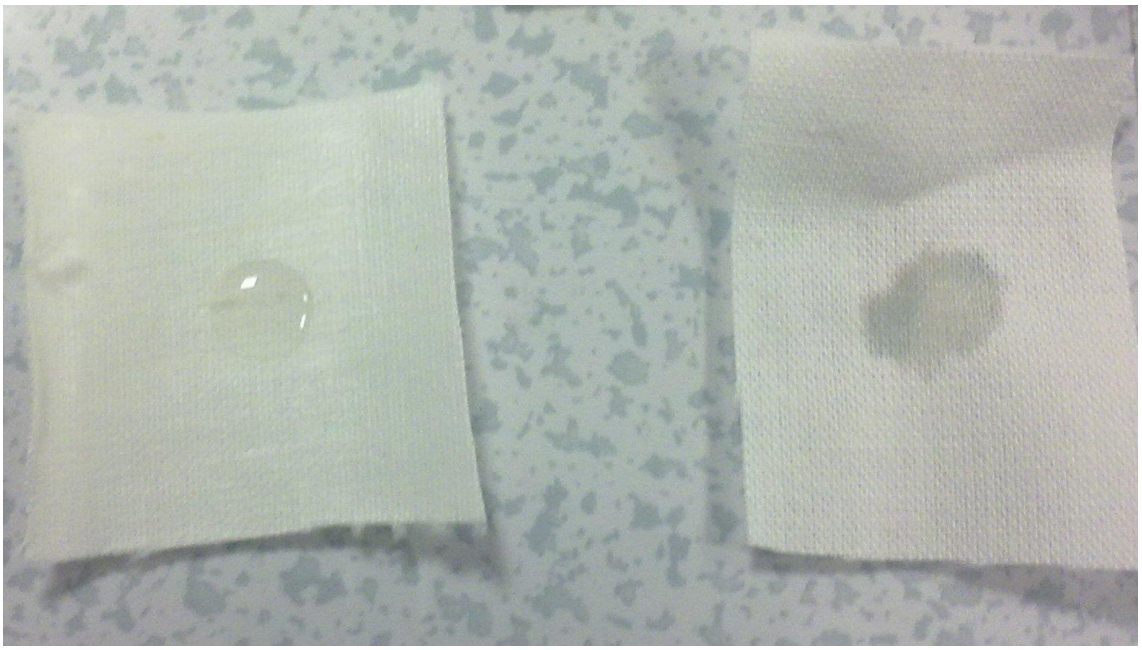


Figure 5.19 Nitric acid placed on coated and uncoated sample

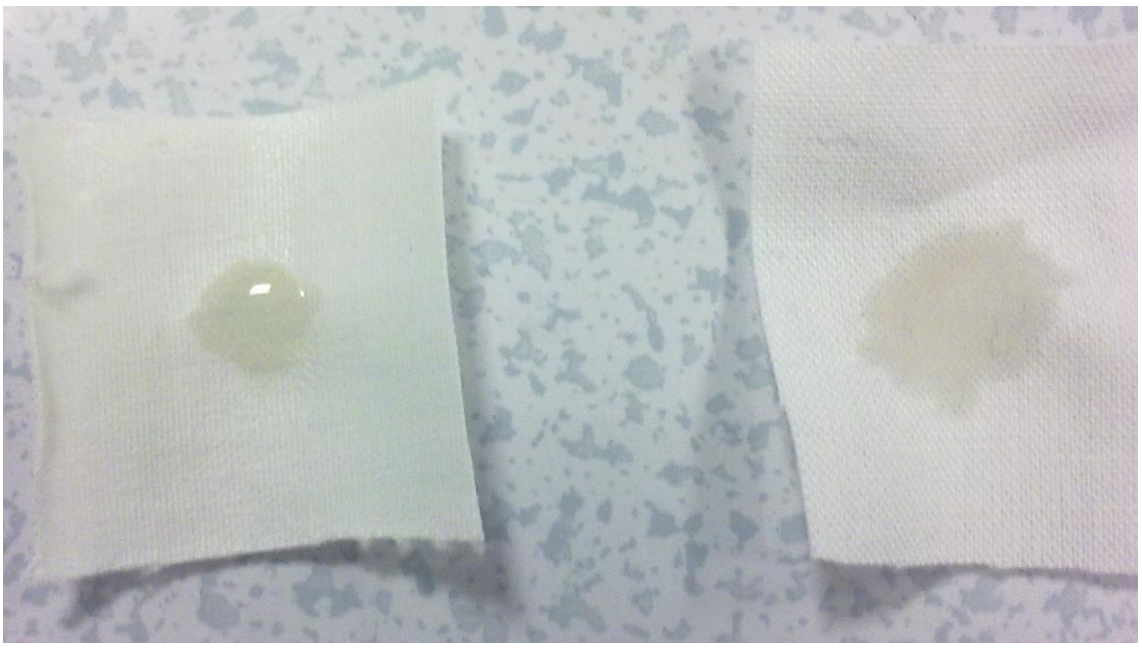


Figure 5.20 Samples after 10 min

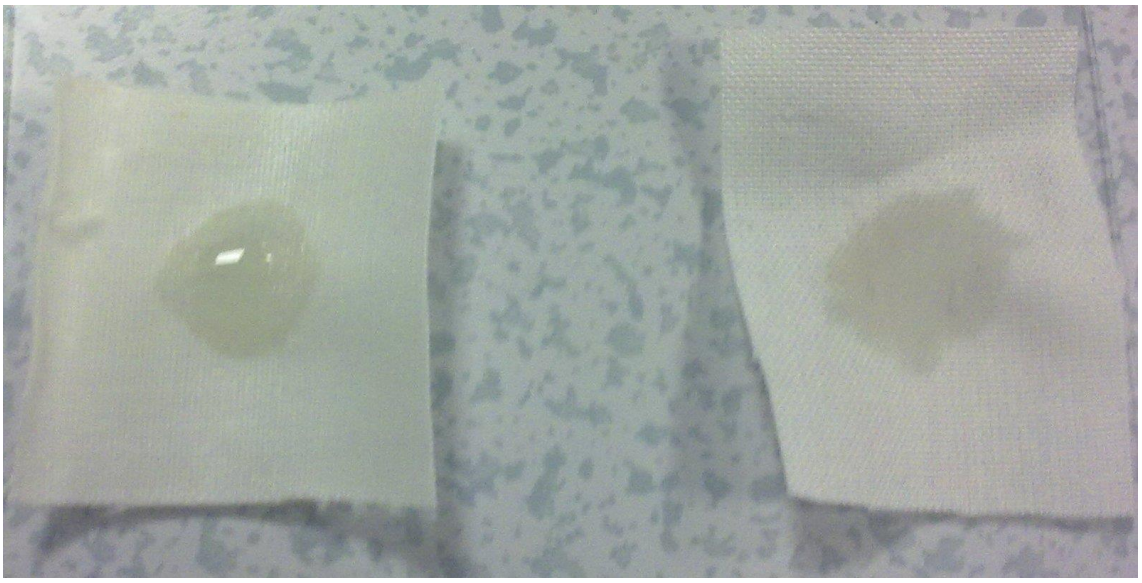


Figure 5.21 Samples after 20 min

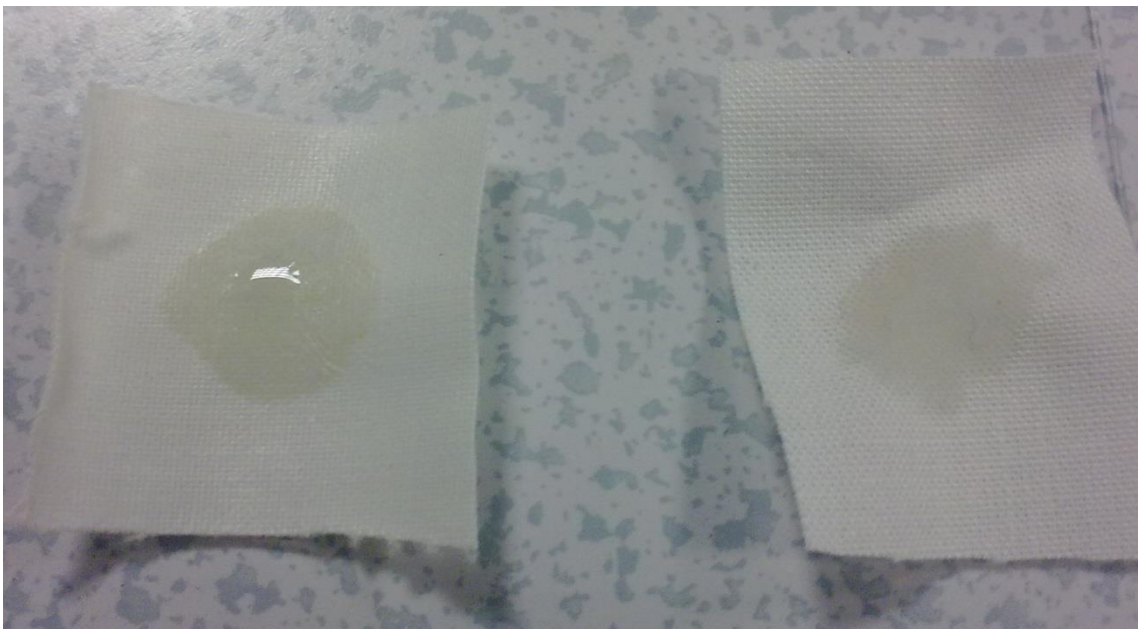


Figure 5.22 Samples after 30 min

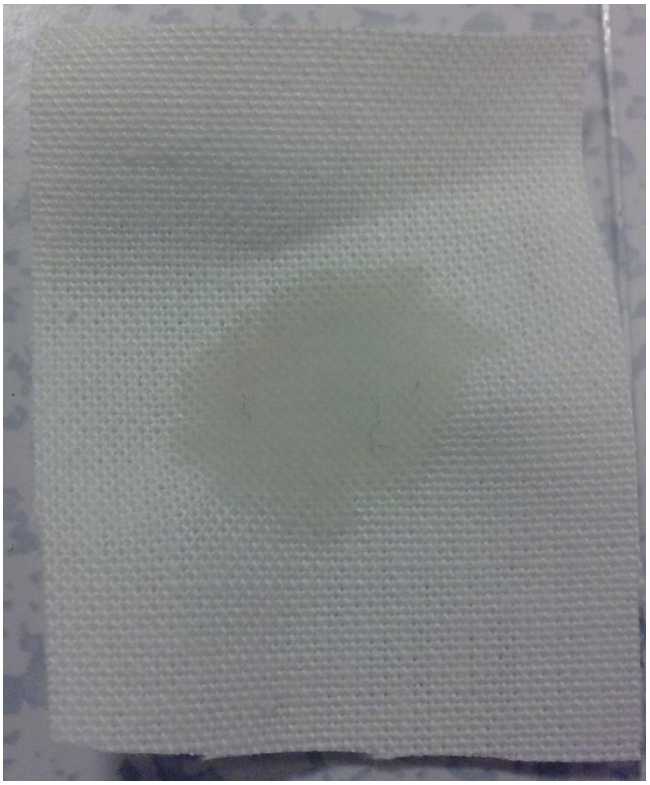


Figure 5.23 Uncoated sample after 30 min exposure of nitric acid

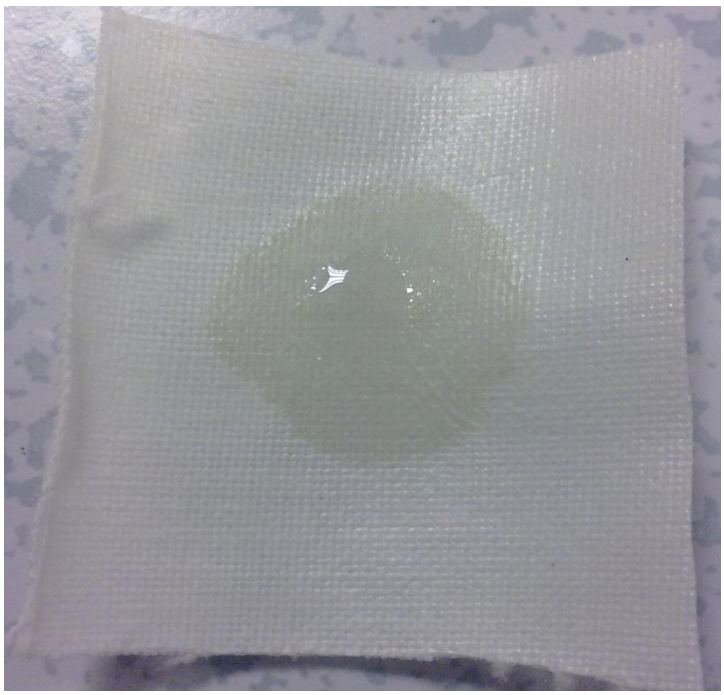
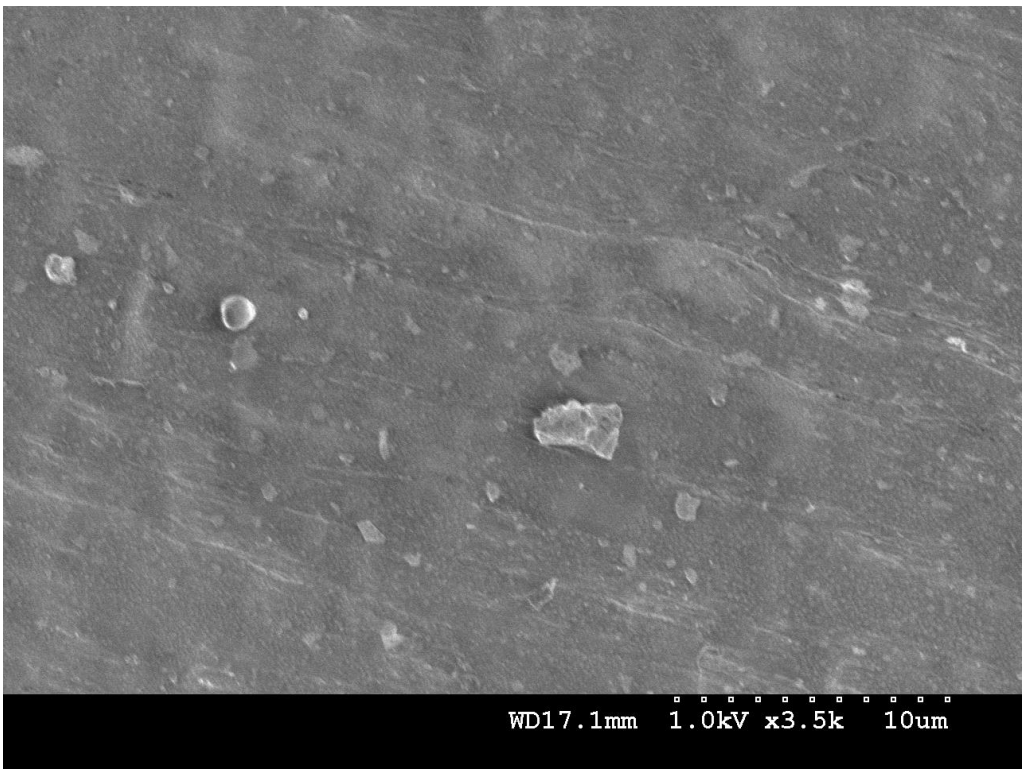


Figure 5.24 Coated sample after 30 min exposure to nitric acid

The coated sample exposed to the nitric acid resisted the acid better than the plain fabric (Figure 5.19 -Figure 5.24). The plain fabric immediately absorbed the nitric acid while the coated sample did not demonstrate any immediate absorption (Figure 5.19). After 10 min the coated sample showed some seepage of acid through the coating (Figure 5.20). This seepage continued to increase until the end of the test at 30 min (Figure 5.21Figure 5.23). Similar to the sulphuric acid test nitric acid seeped through the coating without damaging the coating. To determine the cause of this phenomenon, SEM images of the acid seeped coating area were taken.



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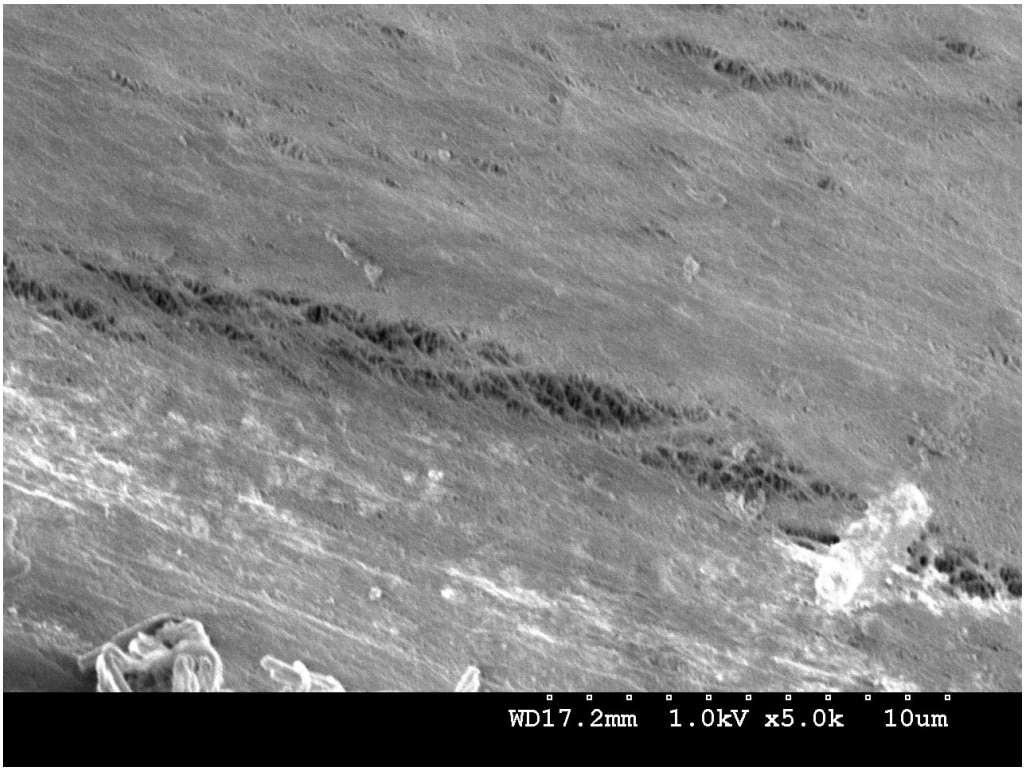

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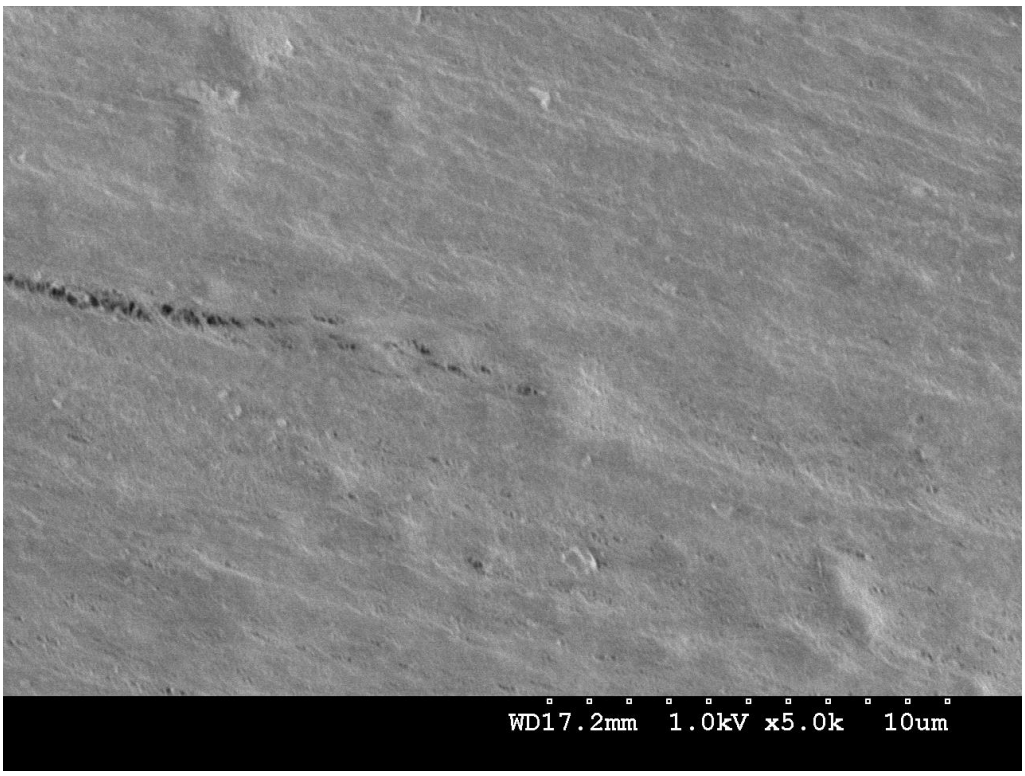

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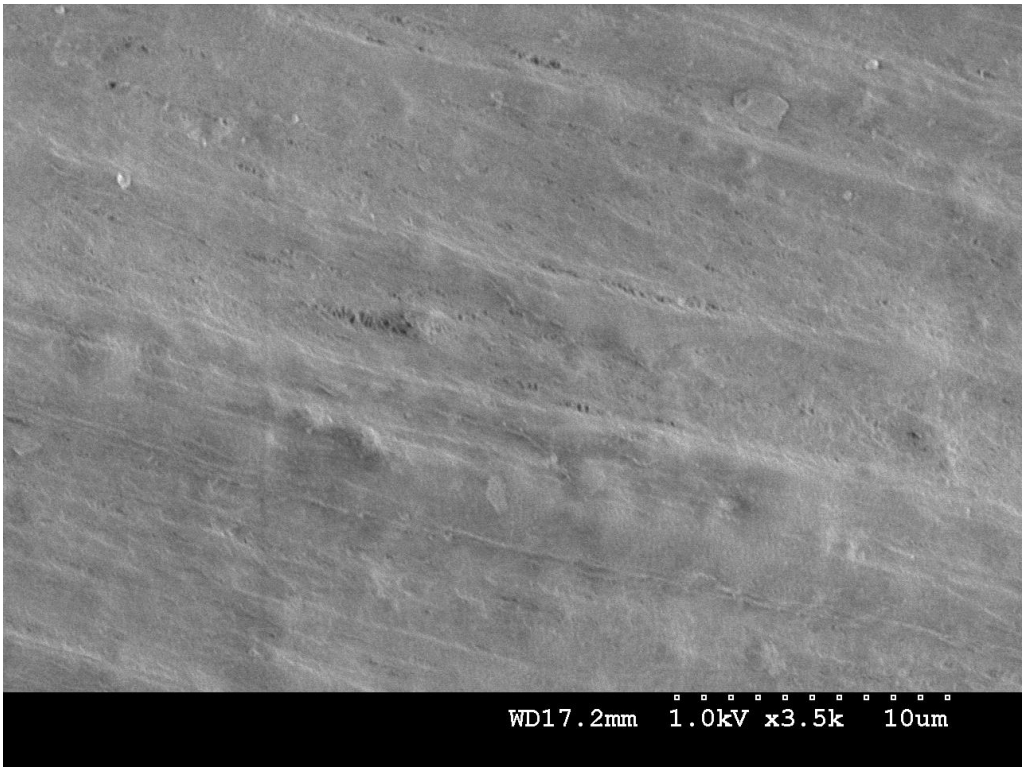

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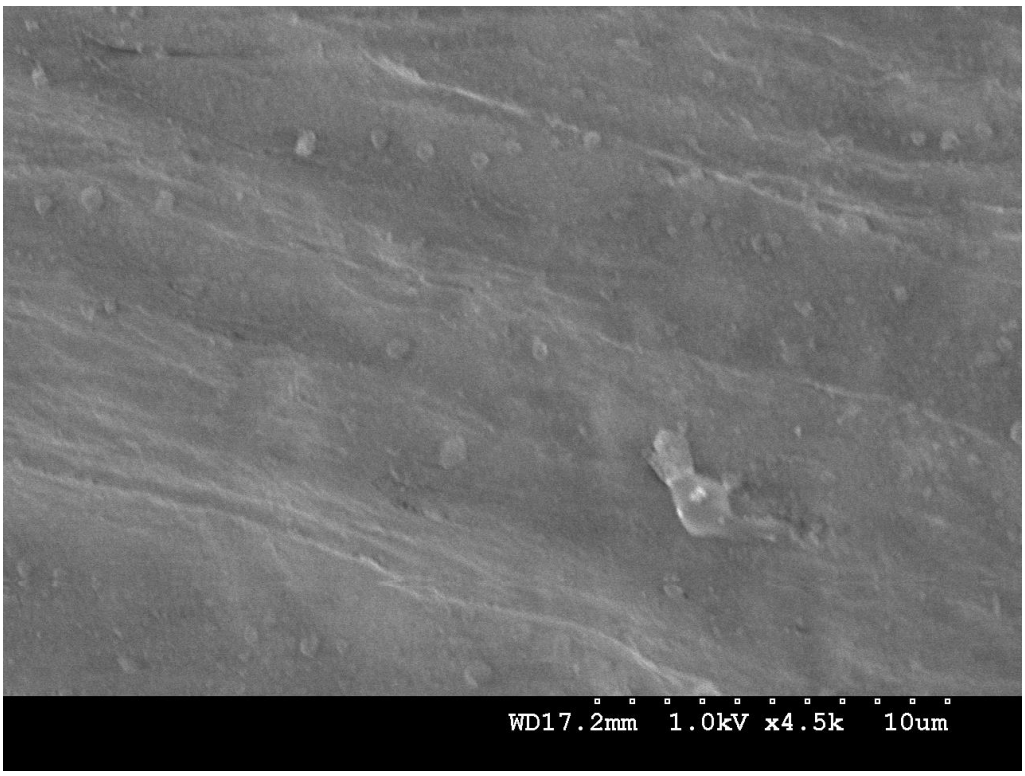

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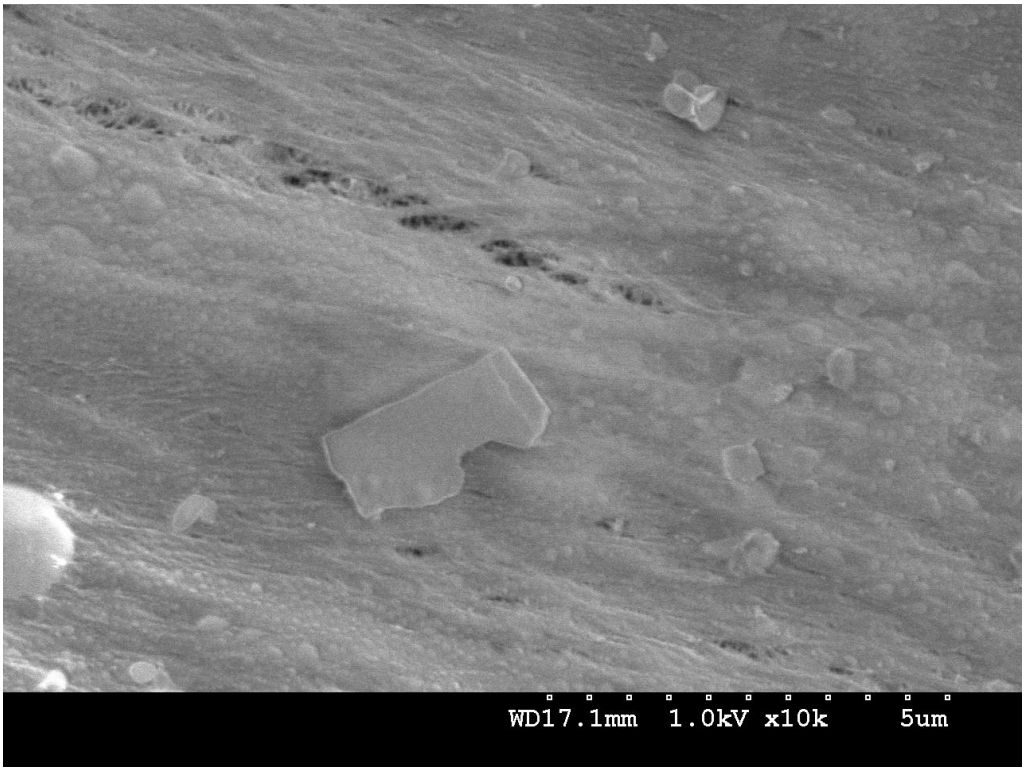

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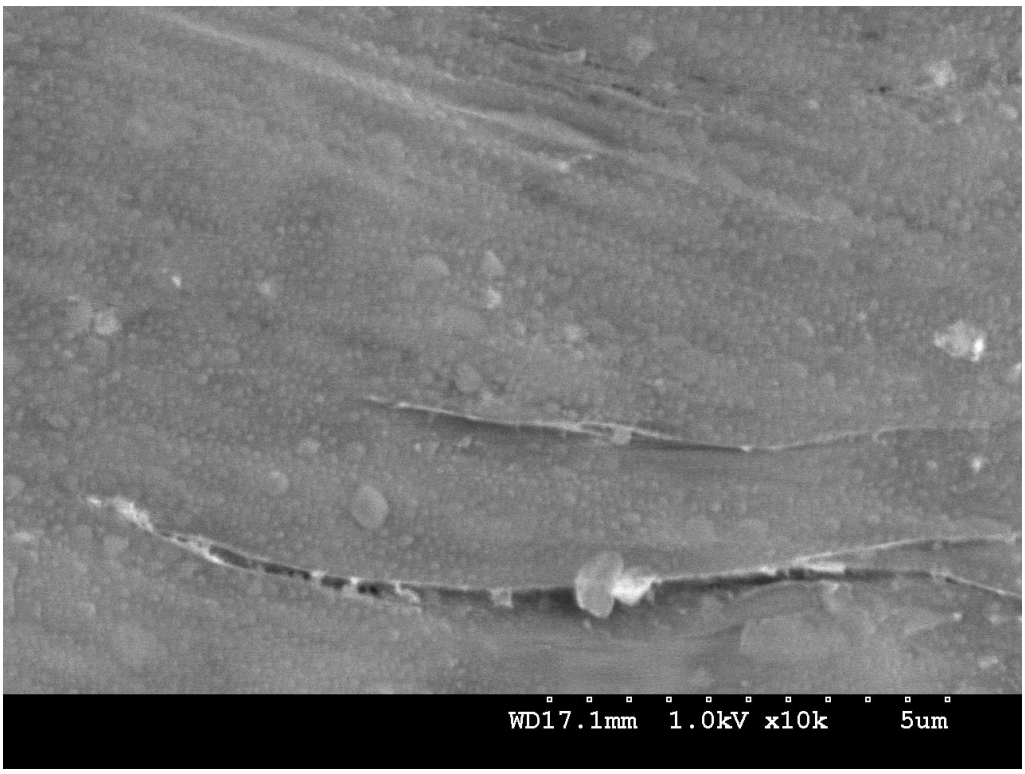

g

Figure 5.25 SEM images of the acid seepage area of the coated sample

The SEM images of the acid seepage area showed small cracks in the coating (Figure 5.25 b-d and f-g). The seepage was probably the result of these small cracks. Some of the samples did not show (Figure 5.25 a and e) any cracks which could be the reason why acid seeped through some points while it did not seep at all through other areas. This also explained the reason why nitric acid with a relatively lower viscosity than the sulphuric acid was easily able to seep through the coating.

The reason why these cracks appeared was the shrinkage of the coating gel. In the case of the fibres when solvent was removed, the diameter of the filament decreased significantly while in the case of the coating this shrinkage caused the cracks.

5.3.3 Strength of Coated Fabrics

The strength of the coated samples was tested on the Instron Tensile Tester. Four sets of samples with different coating thickness and drying condition i.e under tension and without tension were tested. The results of the test are shown in Table 5.1.

Samples	Tensile Stress at Break (N/mm^2)	Maximum Load at Break (N)	Tensile Strain at Break (%)	Tear Resistance (N)
Uncoated fabric	97.04	1101.45	16.23	36.88
Coated sample (0.1 mm thick)	97.53	1107.02	16.36	36.92
Coated sample dried under tension (0.1 mm thick)	95.99	1105.27	15.97	35.78
Coated sample (0.6 mm thick)	101.92	1156.83	18.43	38.32
Coated sample dried under tension (0.6 mm thick)	100.87	1144.92	18.43	37.21

Table 5.1 Strength of coated and uncoated samples

The coated samples with 0.1 mm thick coating showed slight improvement in strength. The samples with the same coating thickness dried under tension showed slight decrease in the strength. Samples coated with 0.6 mm thick coating showed some improvement in the strength. Samples with same coating thickness (0.6 mm) dried under the tension showed slight deterioration in the strength in comparison to the samples dried without tension.

5.4 Summary

The preliminary work was carried out to identify the main parameters and conditions which affect the coating process. The preliminary work indicated the concentration of the polymer in the solution, solvent and phase separation temperature were the main factors which influenced the coating process. The understanding of the main factors lead to the next objective which was the development of the UHMWPE coating method.

A machine was custom designed which allowed to keep the polymer solution above the phase separation temperature during application of coating. UHMWPE was coated onto the cotton fabric by utilising a modified coating machine with heated knife assembly.

The coated fabrics were tested against the concentrated sulphuric and nitric acids. The coated samples showed good resistance to nitric and sulphuric acid. The coated samples also showed improvement in the strength.

The new method of coating has opened new areas of application for UHMWPE, which were off limit before. The high chemical resistance of UHMWPE combined with its very high wear resistance, cut resistance, UV resistance and strength have enormous applications in the form of coating in the fields demanding high performance coatings e.g. motor cycle wear, leisure equipment, military, law enforcements, pond liners, bulk containers, conveyer belts, architectural structures, shoe uppers and linings, chemical resistant apparel etc.

The introduction of UHMWPE coating has also opened a new area of research where the coatings can be applied on the variety of substrate materials to be utilised in variety of applications opening unlimited possibilities.

The next chapter contains the additional work carried out to investigate the integration of the fire retardant in the UHMWPE.

Chapter 6 **Integration of Fire retardant in UHMWPE Fibres**

6.1 Introduction

The newly developed terpene-based gel spinning process consists of an intermediate stage of gel chips, which provided the ability to add additives into the gel before the extrusion. To exploit this advantage extrusion was performed by adding fire retardant in the gel chips before extrusion. The gel was prepared by heating a 5% w/v solution of UHMWPE in terpene with 1% aluminium stearate and 1% 2,6-Di-tert-butyl-4-methylphenol at 130^{o}C for one and half hours. The gel was then left to cool at room temperature overnight. The gel was then converted into the chips (approximate 3mm × 3mm). The fire retardant Phyrolex (Prometheus Developments Ltd) was then added to the chips in different percentages (i.e. 1%, 2%, 5% and 8%) before the extrusion of the gel on the ram extruder. The extrusion was performed on the ram extruder at 150^{o}C. The gel chips with added fire retardant were kept in the ram extruder barrel for 10 min to stabilize the temperature before the extrusion. The extrudate was passed through an air gap then through a water bath followed by winding onto the bobbin at a speed of 2 m/min. The samples were assessed under the SEM microscope to assess the mixing of the fire retardant powder. The mechanical properties of the fibres were also tested.

6.2 Property Characterization of Fire Retardant UHMWPE Fibres

The experiments were conducted by adding different percentage of fire retardant in the gel. The samples with 2%, 5% and 8% fire retardant extruded better than the 1%. An interesting phenomenon was observed where the fibre evenness improved with the increase in the amount of the fire retardant until 8%.

The DSC thermographs of the fibres containing fire retardant were taken to understand the phenomenon of fibres evenness.

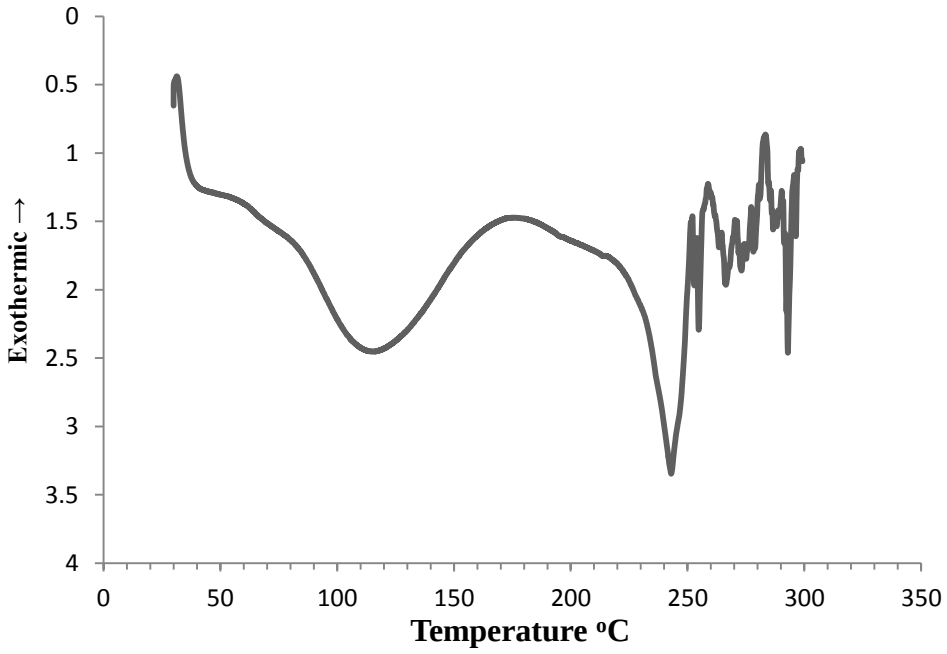

Figure 6.1 DSC thermograph of fire retardant Phyrolex Powder

DSC thermograph of Phyrolex powder shown in Figure 6.1 shows the first very wide peak around 110°C indicating the malting point of the fire retardant. The next peak is shown at 240°C followed by many peaks indicating the degradation of the powder.

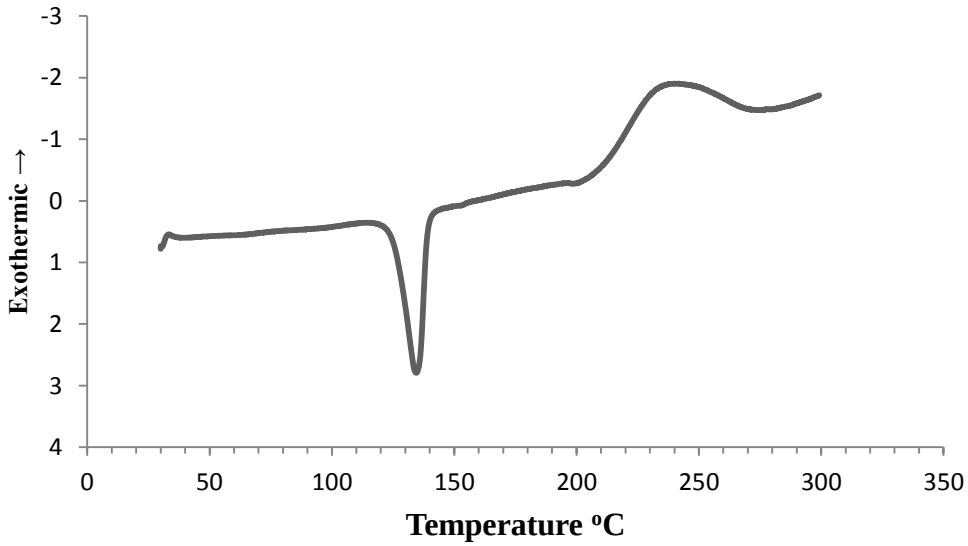

Figure 6.2 DSC thermograph of UHMWPE fibre extruded with 2% fire retardant

The fibres extruded with 2% fire retardant's DSC thermograph showed the first peak at 138°C indicating the melting point of the polymer as shown in Figure 6.2. The peak appeared to be narrow indicating the improved crystallinity of the fibre. There was no presence of a separate peak for the fire retardant powder.

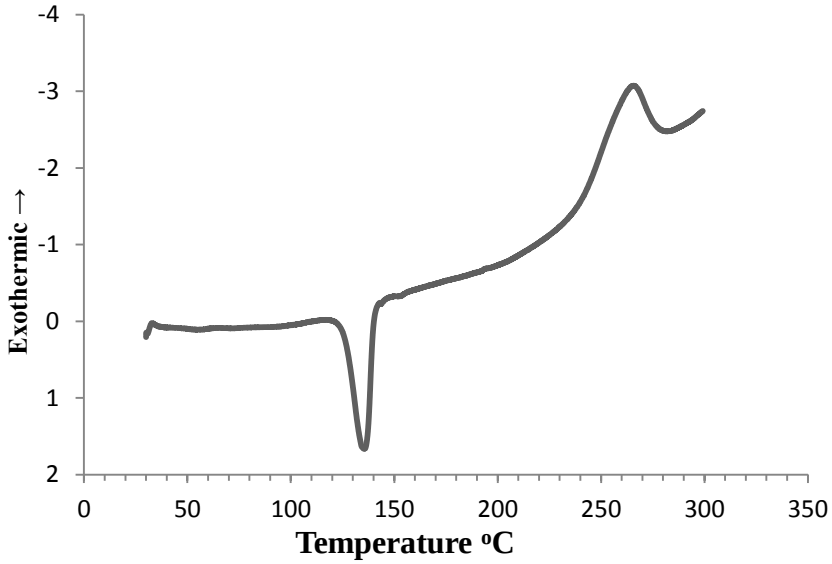

Figure 6.3 DSC thermograph of UHMWPE fibre extruded with 5% fire retardant

The DSC thermograph of the fibres extruded with 5% fire retardant shown in Figure 6.3 showed a peak at 138°C indicating the melting point of the fibre. There was no separate peak for fire retardant indication the good mixing of the fire retardant powder.

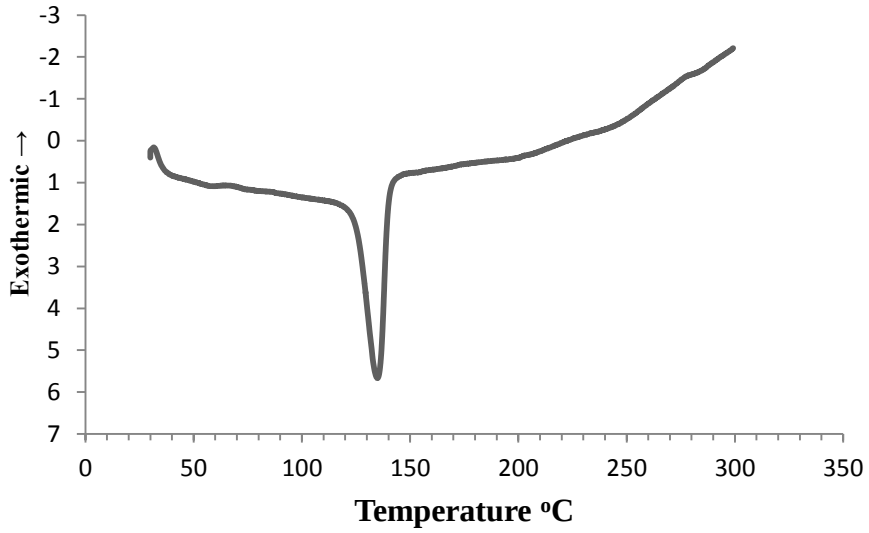

Figure 6.4 DSC thermograph of UHMWPE fibre extruded with 8% fire retardant

The DSC thermograph of the fibres extruded with 8% fire retardant also showed the first peak at 138°C which was due to the melting of the polymer. There was no other peak indicating the good mixing of fire retardant with polymer.

Figure 6.1 shows the DSC thermograph of fire retardant Phyrolex Powder where the first peak appears at 110^{o}C while Figure 6.2-Figure 6.4 show the thermographs of UHMWPE fibres extruded with 2%, 5% and 8% fire retardant which do not demonstrate peaks at 110^{o}C thus indicating adequate mixing of the fire retardant with polymer during the extrusion.

To observe the mixing of the fire retardant in the polymer, SEM images were also taken.

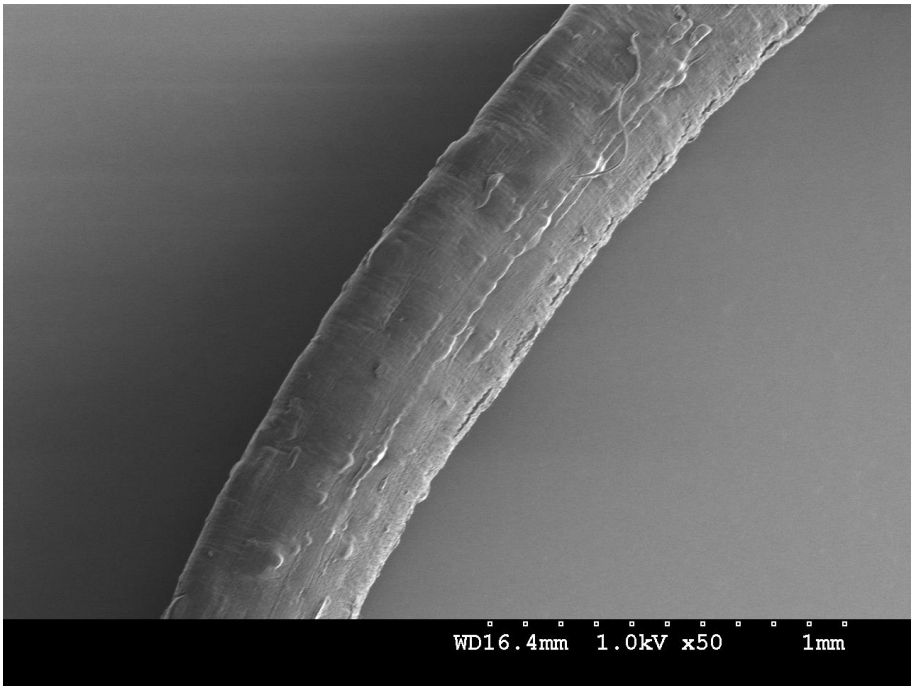

Figure 6.5 SEM Image of UHMWPE fibres extruded with 2% fire retardant

Figure 6.5 shows a 50 times magnified SEM image of a UHMWPE fibre extruded with 2% fire retardant. The image show the fibre is circular with no presence of fire retardant powder as separate entity. To further investigate the blending of the fire retardant with polymer images were taken at higher magnififcation.

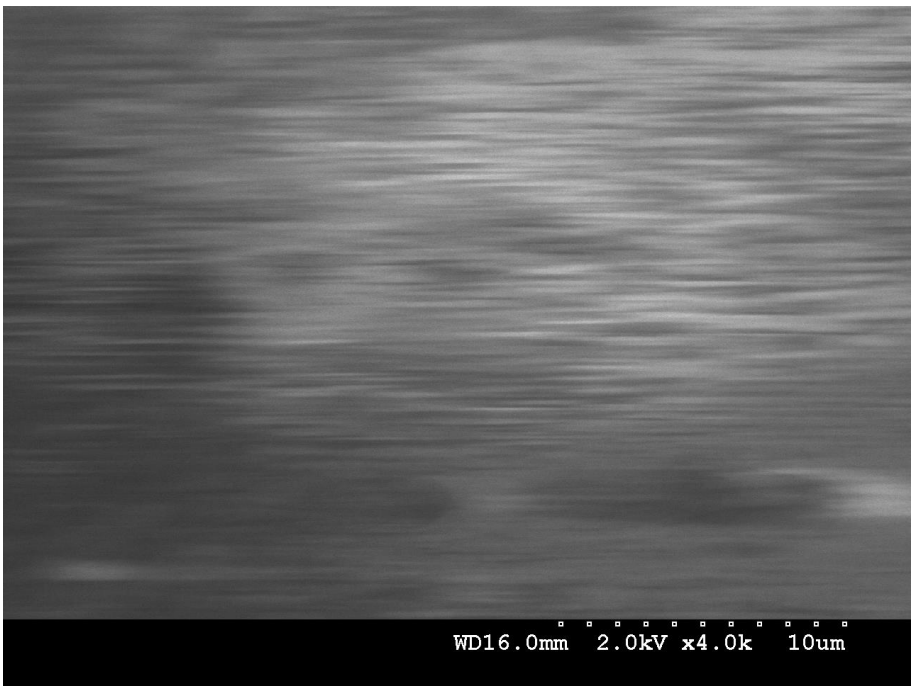

Figure 6.6 SEM Image of UHMWPE fibres extruded with 2% fire retardant

The SEM image of UHMWPE extruded with 2% fire retardant magnified to 4000 time is shown in Figure 6.6. The image shows uniform distribution of fibrils without any present of fire retardant as separate entity indicating the good blending of fire retardant with the polymer.

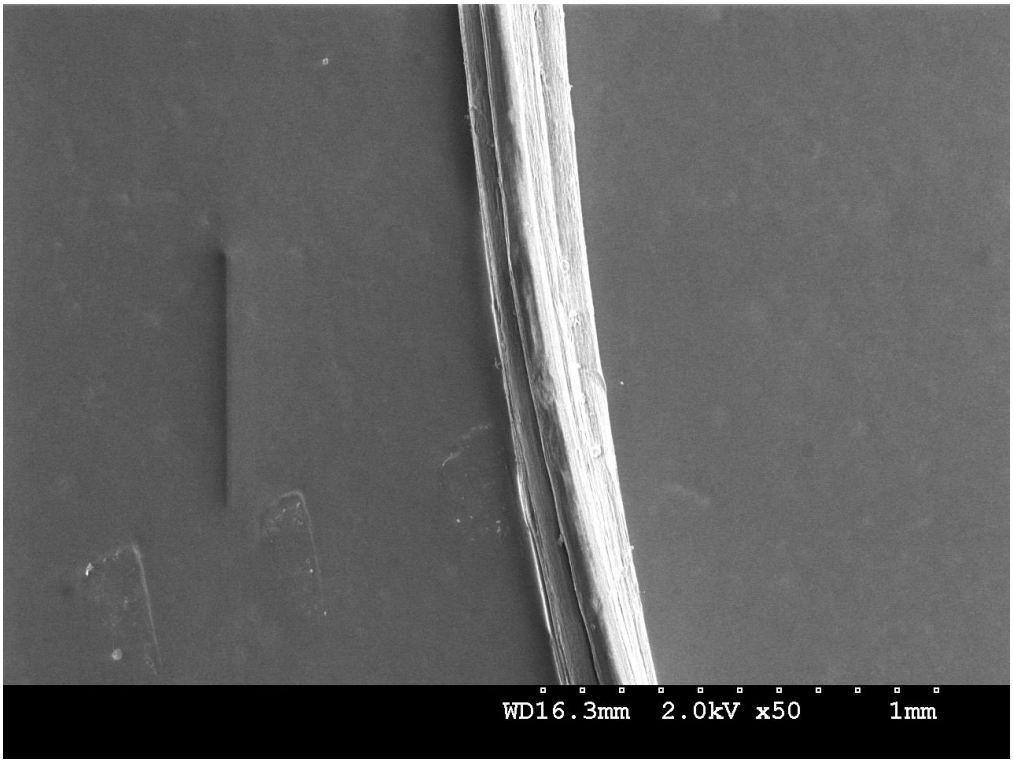

Figure 6.7 SEM Image of UHMWPE fibres extruded with 5% fire retardant

Figure 6.7 shows a SEM image of UHMWPE fibre extruded with 5% fire retardant. The fibre appeared to be multilobal though the extrusion was carried out through a circular die head. The removal of the solvent caused the fibre to turn into the multilobal the phenomenon is explained in the section 4.7. The fibre shows a smooth surface indicating the good blending of the fibre and polymer.

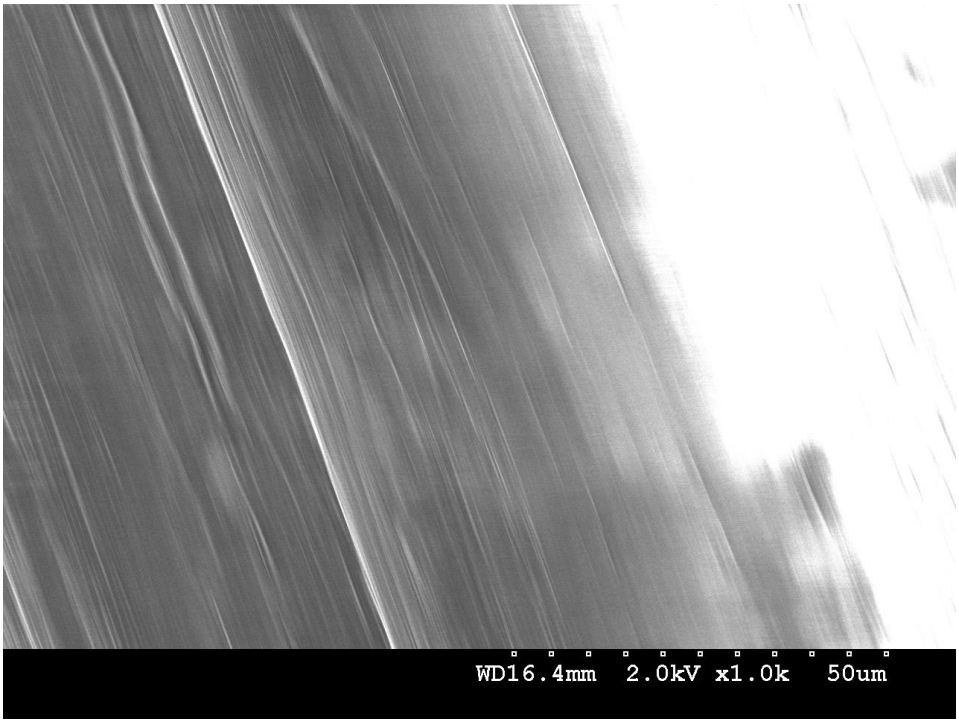

Figure 6.8 SEM Image of UHMWPE fibres extruded with 5% fire retardant

SEM image of the fibre extruded with 5% fire retardant shown in Figure 6.8. The fibre was magnified to 1000 times the image indicates uniform well aligned fibrils without the presence of fire retardant as separate entity.

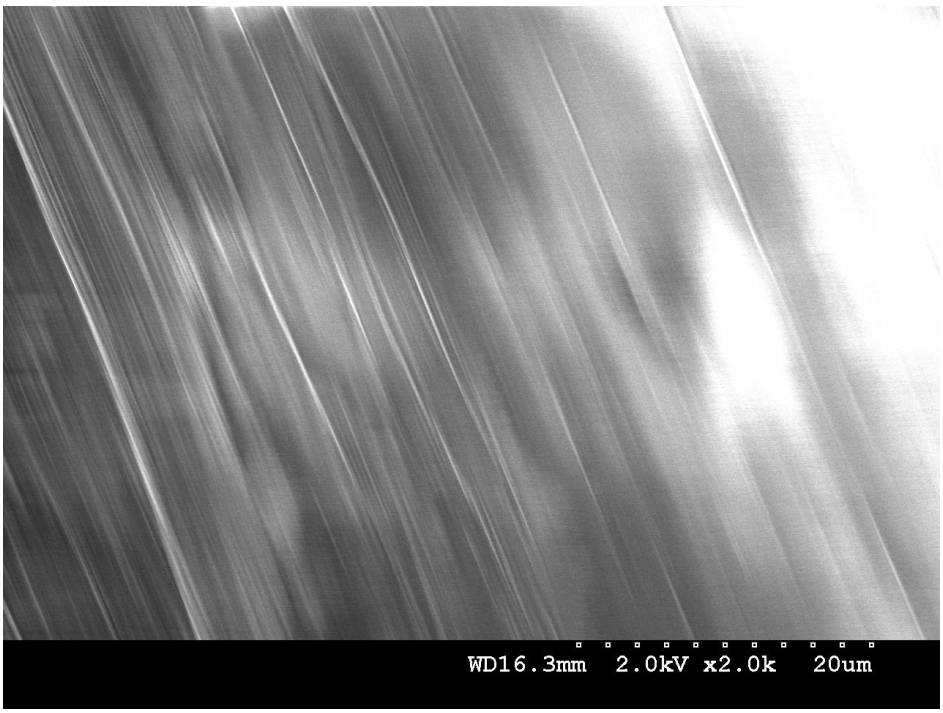

Figure 6.9 SEM Image of UHMWPE fibres extruded with 5% fire retardant

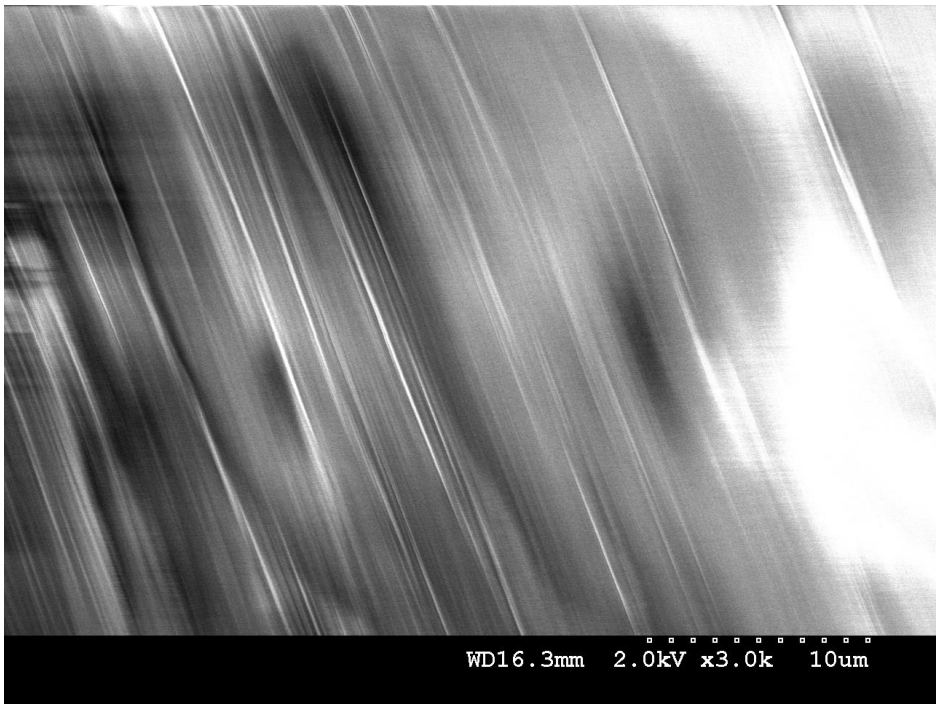

Figure 6.10 SEM Image of UHMWPE fibres extruded with 5% fire retardant

Figure 6.9 and Figure 6.10 show SEM images of UHMWPE fibres extruded with 5% fire retardant. Figure 6.9 shows the image magnified to 2000 times while in Figure 6.10 the fibre is magnified to 3000 times. Both Figure 6.9 and Figure 6.10

indicates the uniform distribution of fibrils and no presence of fire retardant as separate entity.

Figure 6.11 SEM Image of UHMWPE fibres extruded with 8% fire retardant

The fibre extruded with 8% fire retardant is shown in Figure 6.11 the fibre is magnified to 50 times. The figure indicated the same multilobal phenomenon discussed before caused by the contraction of the fibres due to removal of the solvent.

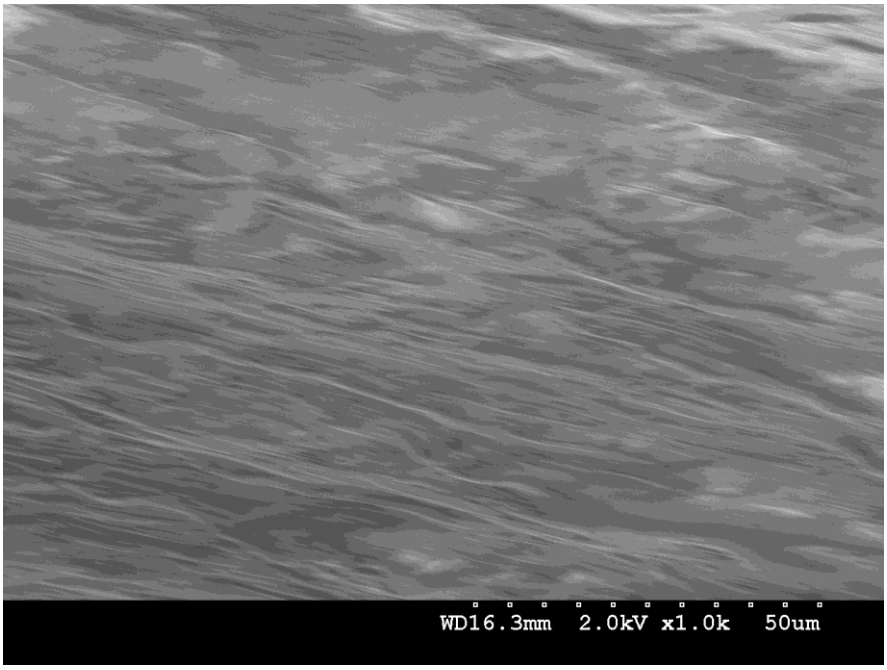

Figure 6.12 SEM Image of UHMWPE fibres extruded with 8% fire retardant

The SEM image UHMWPE fibres extruded with 8% fire retardant magnified to 1000 times is shown in Figure 6.12. The image indicates the fibrils are uniformly distributed without any presence of the fire retardant particle referring to the good mixing of the fire retardant with the polymer.

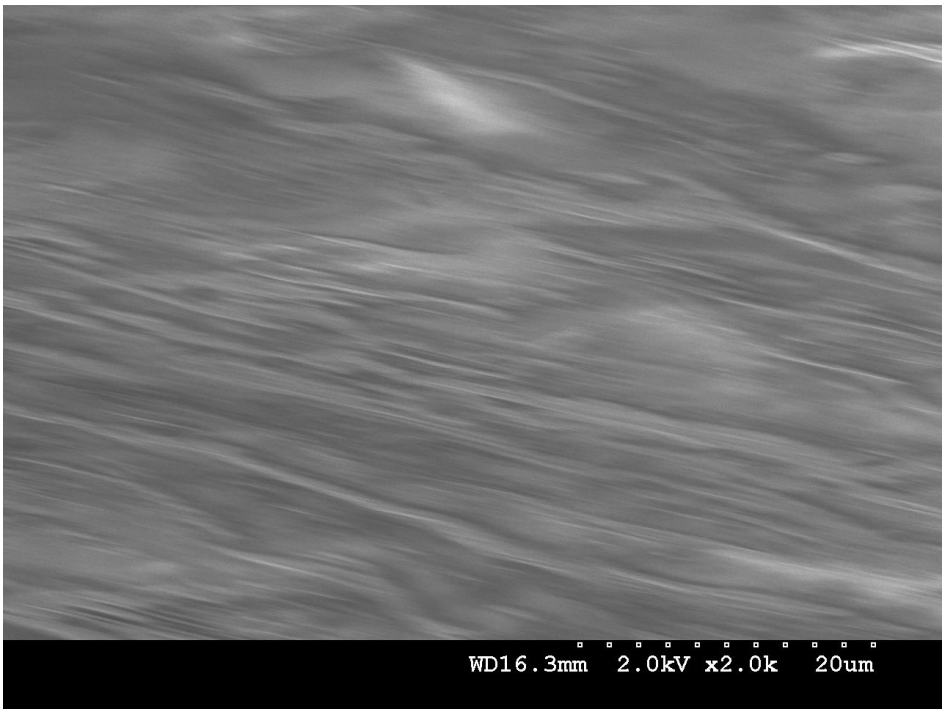

Figure 6.13 SEM Image of UHMWPE fibres extruded with 8% fire retardant

The SEM images of UHMWPE fibre extruded with 8% fire retardant magnified to 2000 times shown in Figure 6.13 indicated the same phenomenon indicated by the previous images the fibrils are uniformly distributed without the presence of fire retardant as a separate entity.

SEM images of the fibres extruded with different percentages of fire retardant did not show the presence of fire retardant powder as a separate entity (Figure 6.5-Figure 6.13). The absence of fire retardant powder as separate entity in SEM images and DSC graphs indicates the adequate mixing of the polymer and fire retardant powder.

Sample	Fibre linear density (dtex)	Tensile strength (N/tex)	Maximum load (N)
Fibres with 2% fire retardant	680	0.036	2.45
Fibres with 5% fire retardant	362	0.115	4.17
Fibres with 8% fire retardant	60	0.54	3.28

Table 6.1 Tensile strength of fire retardant samples

The mechanical properties of the fibres extruded with fire retardant indicated an interesting phenomenon, the strength of the fibres increased with the percentage of the fire retardant as shown in Table 6.1 and Figure 6.14.

Figure 6.14 Fire retardant % vs. strength graph

The reason of improvement in the strength was due to the improvement in the evenness of the fibres extruded with the fire retardant. It is clear from the DSC thermograph of the fire retardant and fibres extruded with fire retardant that the fire retardant and polymer produce a consistent mix which decreases the chance of the thick

and thin areas along the fibre length. As it was discussed previously, the gel presents the problem of sticking to the wall of the die during the extrusion. The addition of the fire retardant reduced this problem. The fire retardant worked as a lubricant by reducing the friction between the gel and metal die [110]. This reduction in the friction can be responsible for the reduced stickiness of gel on the die surface which reduced the occurrence of thick and thin places in the fibres. Other phenomenon, which is responsible for the increase in the strength of the fibre, was the effect of fire retardant as a plasticizer. The positive effect of fire retardant as the plasticizer on the strength of fibres are widely reported [111].

6.3 Summary

Fire retardant integrated UHMWPE fibres were produced by adding the different percentage of fire retardant in the gel. The fire retardant showed good mixing with the polymer. The strength of the fibres increased with the percentage of fire retardant until 8% above that percentage the fibres starts to become uneven. The addition of fire retardant also improved the processability of the fibre by reducing the stickiness of the gel on the die exit.

The next chapter presents the discussion and conclusions of the research work it also contains the suggestions for the future work.

Chapter 7 **Discussion and Conclusions**

7.1 Discussion

UHMWPE fibres superior physical and mechanical properties found their applications in diverse fields. Its ability to provide high strength at lower weight than aramid fibres coupled with its ability to resist mechanical, physical and chemical degrading agents makes it the fibre of choice for applications e.g. bullet resistance, cut resistance, heat resistance, motorcycle wear, protective gloves, chain saw protection, casual wear, sportswear, fishing lines, fishing nets, load-carrying ropes etc [38]. Methods to produce the UHMWPE utilise large quantities of petrochemicals. Since, UHMWPE has very high viscosity it cannot be processed using commonly used melt spinning methods. To overcome this limitation the polymer is first dissolved in a suitable petrochemical (i.e. paraffin, kerosene, decalin, dodecane, p-xylene, tricholobenzene etc) to form a solution. The solution is extruded through an extruder fitted with a die head. The extrudate leaving the die head is passed through a water bath which transforms the extrudate into a gel-like fibres. These gel-like fibres contain a significant amount of spinning solvent which give these fibres its gel-like appearance. To achieve dry fibres, the solvent needs to be removed. This process of solvent removal involves other volatile petrochemical solvents i.e. n-hexane, hexane, cyclohexanone, xylene, gasoline, cholorform, diethyl ether, n-pentane, methylene chloride, trichloro trifluoroethane (TCTFE), n-hexane, dioxane or toluene. The use of high quantities of these hazardous petrochemicals not only as spinning solvents but also for removal makes the process an environmental and health concern. These chemicals also add to the cost of the fibres. Since these chemicals are extracted from fossil fuel, they are not sustainable. There was need to find an environmentally friendly solvent. In order to find such a solvent, different natural oils were considered to find one compatible for spinning. Initial experiments showed the potential of terpene as an alternative to petrochemicals. Fibres were successfully extruded utilising terpene as spinning solvent. As terpene is a natural oil extracted from orange peel it is a waste product of orange juice industry. Since it is from a renewable source (i.e. orange peel) it is sustainable. Experiments showed the fibres spun with terpene oil did not require an extra removal process. If the fibres are spun with petrochemicals these chemicals need to be removed after the extrusion requiring a separate solvent removal stage where more

petrochemicals are used. This ability of the terpene process makes it environmental effect two fold. The elimination of the solvent removal stage also reduces the process cost. A terpene based process reduces the health hazard. The use of terpene oil as an alternative to petrochemicals provides an environmentally friendly process. Since terpene is extracted from orange peel, it is sustainable. It is by-product of the orange juice industry thus does not strain the natural resources and does not put any pressure on food supply. The elimination of the solvent removal process by using the terpene oil considerably reduces the manufacturing cost of the UHMWPE fibres. This process is not only environmentally friendly but it also has potential to be economical. This finding of an alternative solvent paves the way for a new process consisting of a solvent recovery where the terpene could be recycled. Such a process would further reduce the cost of the process and also will make the process more environmentally friendly.

Use of a solvent to extrude the UHMWPE is inevitable due to its very high viscosity. The solvent does not play any role other than a medium in which polymer is dissolved to achieve the required viscosity for the extrusion. After the extrusion, the solvent is removed from the fibre. The solvent does not directly contribute to improve the properties of the fibres. Different researchers used different percentages of the solvent to extrude the fibres. Contradictory conclusions (i.e. whether strength increases or decreases with the increase of polymer percentage) were reported in the literature about the effect of percentage of the polymer on the fibre strength. It was necessary to investigate whether strength increases with the increase in percentage or vice versa for the newly developed process. Since the solvent itself does not directly contribute to fibre strength, the excessive use of solvent only increases the cost of the process without providing any gain in strength. To investigate the effect of the polymer percentage on the strength, an experimental design was performed. The results of the experimental design showed the strength of the fibres is directly proportion to the percentage of the polymer in the solution. These results agreed with the previous reported findings of Proversek [4]. Hence, the fibres could be manufactured utilising the least amount of solvent without compromising the strength of the fibres. This would significantly reduce the cost of the processing by utilising less solvent.

The energy consumption is one of the major cost factors associated with any process. In the case of the previous processing methods of UHMWPE fibres, there was a considerable difference in the processing temperatures. The processing temperature was greatly dependant on the solvent used, the more volatile solvents required lower

temperatures while the solvents with low volatility needed to be processed with higher temperatures. To find the most appropriate processing temperature for the terpene process an experimental design was performed. The results indicated the polymer could be processed at a relatively lower temperature than the most of the petrochemicals reported in the previous studies. Hence, the fibres can be produced by utilizing terpene at lower temperature than the petrochemicals thus reducing the processing cost by saving energy. This reduction in the consumption of the energy also has positive environmental effects. It not only reduces the cost of the process but also puts less pressure on the energy resources.

Ultrasound has been widely used for the ultrasound-induced polymer scission in which the polymer is exposed to ultrasound, which first causes the extension of polymer under the influence of ultrasound followed by scission. This property of ultrasound to extend the polymer chains was thought to have potential in achieving better oriented fibres. The extension of polymer chains disentangles them and reduces the chances of chain entanglement, which results in the stronger fibres. An apparatus was designed to treat the UHMWPE polymer gel with ultrasound prior to extrusion. The fibres showed improvement during the extrusion process. The fibres extruded were found to be more even. The SEM images further showed better fibril alignment to the fibre's axis. The comparison of the DSC thermograph of treated and untreated samples showed a difference between two graphs. The untreated sample showed a very uneven graph referring to polymer chain defects while the treated samples showed much more even graphs referring to well aligned polymer chains. The treated samples also showed a slight increase in the melting point of the fibres which is an indication of increased crystallinity. The measurement of the orientation indicated the improvement in the orientation of the fibres treated with ultrasound. The samples showed better orientation at all draw ratios than the controlled untreated samples. Hence, the orientation of the fibres can be increased by treating the gel with ultrasound before extrusion. This was a new finding as there is no mention of the utilization of ultrasound to improve the orientations of the fibres in the literature. The orientation of the polymer chains plays the most important role in the fibre strength of UHMWPE. Hence, the improved orientation means improved strength. It is suggested here a machine equipped with the sonication unit installed before the die head could significantly improve the orientation of the fibres, which ultimately will result in stronger fibres. The benefit of the ultrasound treatment is not only limited to the UHMWPE fibres it has potential in

improving orientation of other fibres. Further work needs to be done to investigate the extent of improvement in other fibres using ultrasound energy.

The published literature had no mention of the UHMWPE as coatings on fabrics. However, the superior physical and chemical properties of the UHMWPE could be of great use if applied to fabrics. The reason may be the difficult application of the material or having no advantages over standard procedures. The chemical testing of the polymer showed resistance to acids so it was more likely the application of the coating which prevents its use. The initial experiments showed the coating cannot be achieve by utilising conventional coating methods. The process developed in this research successfully achieved the coating. The limitation of gel phase separation was overcome by designing a new knife having heaters adhered to it to keep the coating paste above its phase separation temperature. The coated samples demonstrated resistance to acids (i.e. sulphuric acid and nitric acid). The SEM images of coatings showed an acceptable uniformity although the images also demonstrated the presence of cracks in the coating due to the shrinkage of coating due to evaporation of the solvent and the inability of the fabric to shrink.

Although there was some success in producing low cost chemical resistant fabrics, further works needs to be done to overcome the problem of cracking due to differential shrinkage. Once this is achieved, relatively cheap, chemically resistant fabric would be available for a range of applications such as personal protective equipment for the rescue, emergency and military services, anti-spillage barriers etc.

The strength of UHMWPE is 40% stronger than the aramid fibres. Due to its superior strength, it is widely used in protective clothing. Although it has superior physical and chemical properties it is not flameproof. This lack of fire retardant property excludes UHMWPE to be considered in the applications involving exposure to fire instead of its superior properties in other areas. In the present work fire retardant integrated UHMWPE fibres were produced, fire retardant was added in different percentages (i.e. 2%, 5% and 8%) to the polymer gel. The fibres produced were uniform without any weak places which indicated the uniform mixing of the fire retardant. An interesting phenomenon was also observed the strength of the fibres increased with the increased percentage of fire retardant until 8%; above that fibres started to lose their uniformity resulting in weak places. This increase in the strength was thoroughly investigated. It was found from the SEM images and DSC thermograph

that the fire retardant worked as a lubricant by reducing the friction between the gel and metal die [110]. This reduction in the friction was responsible for the reduced stickiness of gel on the die surface which reduced the occurrence of thick and thin places in the fibres. This reduction in the thick and thin places improved the strength of the fibres. The experiment showed the potential of the UHMWPE to be extruded with the fire retardant hence imparting fire retardant properties on the fibres, although further work needs to be done to investigate improvement in the fire retardant properties of the fibres. This will open a new avenue for the application of the fibres. As shown in the experiment, the fibre does not compromise the strength and shows the potential to have fibre with better fire retardant properties without compromising its physical properties. This could lead to the application of UHMWPE fibres in the fields which were off-limit before. It shows the potential for a police vest which is not only bullet proof but also works as fire protection.

7.2 Conclusions

1) The solvents previously used for gel spinning were petrochemicals and therefore not from a sustainable resource and put pressure on the limited supply of fossil fuel. Terpene, which is a natural oil extracted from orange peel, can replace the petrochemicals previously used in the processing of UHMWPE. As a natural oil, it is obtained from renewable resources i.e. a by-product from the orange juice industry. Unlike other sustainable alternative to petrochemical, e.g. biodiesel which are extracted from edible products it is extracted from the orange peel hence it in not only sustainable it also does not put pressure on the human food supply.

2) The terpene-based process utilises the terpene instead of petrochemicals since the terpene is biodegradable the disposal of terpene does not requires special treatments, hence reducing the cost involved to dispose it.

3) The terpene-based process is more user friendly than the previously reported process due to the utilisation of the terpene as solvent instead of petrochemicals. FDA (food and drug administration of United States) has given the terpene GRAS (generally recognised as safe) status. Terpene is not considered a carcinogen, a developmental toxicant or mutagenic. The safer nature of the terpne makes the process less hazardous to the people working in

the production of the fibres. Hence, making the process safer than the previous processes.

4) The petrochemical solvents used in traditional gel spinning of UHMWPE works only as a medium to assist in the spinning of the fibres from polymer powder. After fibres have been extruded, the solvents need to be removed which involves the use of a secondary petrochemical solvent. In terpene-based gel spinning process, the extraction of solvent takes place during the water quenching of the fibre and does not therefore require a separate removal process hence eliminates the need for an extraction stage employing additional solvents. The elimination of the secondary solvent not only reduces the cost associated with it. It also eliminates the other three major concerns regarding sustainability, environmental and health hazards. The complete elimination of the extraction stage also eliminates the labour and energy costs associated with this stage.

5) The results of experimental design indicated the most important factors which influence the strength of the fibres in the newly developed terpene based process were concentration followed by the combination of particle size and concentration. The third most important factor was the combination of concentration and heating time followed by heating time and combination of temperature and concentration. The particle size and temperature did not show any significant effect.

6) From the experiment involving ultrasonically treated gel, it was found that this treatment improves the orientation of the fibrils which leads to improvements in the fibre strength. This improvement in orientation also reduces the fibril entanglement and polymer chain entanglement which improves the evenness of the fibre and reduces breakage during processing. This improvement in the alignment of polymer chains by ultrasonic treatment has opened a new avenue for research, which can lead to the improvement of the fibre strength in other polymers as well.

7) The preliminary studies showed the concentration of the polymer in the solution, solvent and phase separation temperature were the main factors which influenced the coating process of UHMWPE.

8) The development of UHMWPE coating process on to the fabric has opened a new area of application for UHMWPE which was off-limit before. The process developed in the research involves a custom designed coating machine, which allows the coating of the UHMWPE onto the fabric. The coatings showed good resistance to sulphuric and nitric acids. The coating also showed improvement in the strength of the fabric. The high chemical resistance of UHMWPE combined with its very high wear resistance, cut resistance, UV resistance and strength have enormous applications in the form of coating in the fields demanding high performance coatings e.g. motorcycle wear, leisure equipment, military, law enforcements, chemical resistant apparel, anti-spillage barriers, sportswear, sports equipments etc. The development of coating process has also opened the new avenue for research where the UHMWPE coatings can be applied on variety of substrate to be utilised in different applications.

9) UHMWPE fibres were produced with fire retardant integrated into them. The fibres showed good uniformity. SEM and DSC thermographs showed uniform mixing of fire retardant and UHMWPE. The comparison of fibres produced with different fire retardant percentage demonstrated the strength of the fibres increased with the increased fire retardant percentage until 8% above that the fibres started to become uneven and difficult to extrude.

7.3 Recommendation for Future Work

a) Fibres derived from the terpene gel can be drawn to investigate the maximum strength achievable.
b) The crystallinity of the fibres produced from the terpene gel could be studied at different draw ratios.
c) Improvement in the orientation of other polymers due to the ultrasonic treatment can be investigated.
d) Coating of UHMWPE on other substrate fabrics can be studied.
e) The fire retardant properties of the fibre can be investigated.

f) Screw extrusion of terpene based UHMWPE solution can be investigated by employing different screw designs.

Reference

[1] T. I. limited, “High strength fibres and fabrics,” *Performance Apparel Markets*, no. 3, pp. 16-31, 2002.

[2] C. Hinton, "DuPont builds $500 million Kevlar plant in SC," *The wall street journal*, http://articles.marketwatch.com/2007-12-18/news/30750775_1_kevlar-dupont-spruance-plant, 2007].

[3] J. G. Lavin, *High-performance fibres*, J. W. S. Hearle, ed., pp. 156-188: Woodhead publishing limited.

[4] D. C. Prevorsek, "Spectra:The latest entry in the field if high-performance fibers," *Handbook of fiber science and technology*, M. lewin, ed., pp. 25-27, New York: Marcel Dekker 1996.

[5] G. C. Weedon, and T. Y. Tam, "Properties and applications of extended chain polyethylene," *High performance fibers textiles and composites, UMIST*, 1985.

[6] S. Rebouillat, "Aramids," *High-performance fibres*, J. W. S. Hearle, ed., pp. 23-61: Woodhead, 2001.

[7] Author ed.^eds., “Lightweight ballistic composites military and law-enforcement applications,” Cambridge: Woodhead publishing 2006.

[8] J. Smook, and A. J. Pennings, “Elastic flow instabilities and shish-kebab formation during gel-spinning of ultra-high molecular weight polyethylene,” *Journal of Materials Science*, vol. 19, no. 1, pp. 31-43, 1984.

[9] Y. Zhang, X. Changfa, J. Guangxia *et al.*, “Study of gel-spinning process of Ultra-High molecular weight polythylene,” *Journal of Applied Polymer Science*, vol. 74, no. 3, pp. 670-675, 1999.

[10] A. J. Pennings, J. Smook, J. d. Boer *et al.*, “Process of preparation and properties of Ulra-High Strength Plyethylene fibers ” *Pure and Applied Chemistry*, vol. 55, no. 5, pp. 777-798, 1983.

[11] E. P. G. Gohl, and L. D. Vilensky, *Textile science,* second ed., Melbourne, Australia: Longman Cheshire Pty Limited, 1983.

[12] A. Calhoun, and A. J. Peacock, *Polymer Chemistry: Properties and Applications*: Hanser Gardner Publication inc., 2006.

[13] J. L. Throne, *Understanding Thermoforming*, second ed.: Hanser Gardner Publications inc., 2008.

[14] L. Pauling, *General Chemistry,* Third ed., NY: Dover Publication inc., 1988.

[15] D. M. Teegarden, *Polymer Chemistry: Introduction to an Indispensable Science*: National Science Teachers Association Press, 2004.

[16] W. Binder, "Hydrogen Bonded Polymers," *Advances in polymer science*: Springer, 2007.

[17] S. Sekhri, *Texbook of Fabric Science: Fundamentals to Finishing*, New Delhi: PHI 2011.

[18] A. Keller, "Polymer single crystals," *Polymer,* vol. 3, pp. 393-421, 1962.

[19] D. C. Bassett, and A. Keller, "Similarities between the behavior of single crystals and that of the bulk material on annealing in polyethylene," *Journal of Polymer Science,* vol. 40, no. 137, pp. 565-568, 1959.

[20] E. S. Clark, and L. S. Scott, "Superdrawn crystalline polymers: A new class of high-strength fiber," *Polymer Engineering & Science,* vol. 14, no. 10, pp. 682-686, 1974.

[21] E. W. Fischer, H. Goddar, and W. Piesczek, "Relationship between structure of drawn polymers and molecular motion," *Journal of Polymer Science Part C: Polymer Symposia,* vol. 32, no. 1, pp. 149-193, 1971.

[22] D. C. Prevorsek, P. J. Harget, R. K. Sharma *et al.*, "Nylon 6 fibers: Changes in structure between moderate and high draw ratios," *Journal of Macromolecular Science, Part B,* vol. 8, no. 1-2, pp. 127-156, 1973.

[23] A. Peterlin, “Radical formation and fracture of highly drawn crystalline polymers,” *Journal of Macromolecular Science, Part B,* vol. 6, no. 4, pp. 583-597, 2012/07/30, 1972.

[24] R. G. C. Arridge, P. J. Barham, and A. Keller, “Self-hardening of highly oriented polyethylene,” *Journal of Polymer Science: Polymer Physics Edition,* vol. 15, no. 3, pp. 389-401, 1977.

[25] S. L. Kwolek, *Optically anisotropic aromatic polyamide dopes*, USA Patent no.3671542, to E. I. du Pont de Nemours and Company, 1972.

[26] J. R. Schaefgen, T. I. Bair, J. W. Ballou *et al.*, "Rigid chain polymers: properties of solutions and fibres," *Ultra-High Modulus Polymers*, A. Ciferri and I. M. Ward, eds.: Applied Science Publishers, 1979.

[27] Toyobo. "Dyneema® Properties", 20 June, 2012; http://www.toyobo-global.com/seihin/dn/dyneema/seihin/tokutyou.htm.

[28] L. M. Fang, P. Gao, and X. W. Cao, “Temperature window effect and its application in extrusion of ultrahigh molecular weight polyethylene,” *eXPRESS Polymer Letters,* vol. 5, no. 8, pp. 674-684, 2011.

[29] A. J. Waddon, and A. Keller, “A temperature window of extrudability and reduced flow resistance in high-molecular weight polyethylene; interpretation in terms of flow-induced mobile hexagonal phase,” *Journal of Polymer Science Part B: Polymer Physics,* vol. 28, no. 7, pp. 1063-1073, 1990.

[30] T. Nakajima, "Advanced fiber spinning technology," Woodhead, 1994.

[31] D. M. Bigg, “A review of techniques for processing ultra-high modulus polymers,” *Polymer Engineering & Science,* vol. 16, no. 11, pp. 725-734, 1976.

[32] P. J. Barham, and A. Keller, “The achievement of high-modulus polyethylene fibres and the modulus of polyethylene crystals,” *Journal of Polymer Science,* vol. 17, no. 9, pp. 3, 1979.

[33] C. E. Meihuizen, A. J. Pennings, and A. Zwijnenburg, *Process for continuous preparation of fibrous polymer crystals*, USA Patent no.4137394, to Stamicarbon, B.V., 1979.

[34] S. Kavesh, D. C. Prevorsek, and D. G. Wang, *Production of high strength polyethylene filaments*, USA Patent no.4356138, to Allied Corporation, 1982.

[35] A. Zwijnenburg, and A. J. Pennings, "Longitudinal growth of polymer crystals from flowing solutions III. Polyethylene crystals in Couette flow," *Colloid & Polymer Science*, vol. 254, no. 10, pp. 868-881, 1976.

[36] J. C. M. Torfs, and A. J. Pennings, "Longitudinal growth of polymer crystals from flowing solutions. VIII. Mechanism of fiber formation on rotor surface," *Journal of Applied Polymer science*, vol. 26, no. 1, pp. 303-320, 1981.

[37] A. J. Pennings, and K. E. Meihuizen, "Polyethylene fibres with ultra-high modulus and strength produced by flow-controlled crystallisation," *Ultra-High Modulus Polymers*, A. Ciferri and I. M. Ward, eds.: Applied Science Publishers, 1979.

[38] J. J. V. Dingene, "Gel-Spun high-performance polyethylene fibers," *High Performance Fibers*, J. W. S. Hearle, ed., pp. 62-92: Woodhead, 2001.

[39] P. Smith, and P. J. Lemstra, *Process for making polymer filaments which have a high tensile strength and a high modulus*, USA Patent no.4344908, to Stamicarbon, 1982.

[40] S. Kavesh, *Preparation of solution of high molecular weight polymers*, USA Patent no.4784820, to Allied signal, 1988.

[41] W.-L. Chen, D.-M. Lee, L.-T. Chen *et al.*, *Process for producing high tenacity and high modulus polyethylene fibers*, USA Patent no.5342567, to Industrial Technology Research Institute, 1994.

[42] P. Smith, P. J. Lemstra, R. Kirschbaum *et al.*, *Process for the production of polymer filaments having high tensile strength*, USA Patent no.4436689, to Stamicarbon B.V., 1984.

[43] S. Kavesh, and D. C. Prevorsek, *Producing high tenacity, high modulus crystalline article such as fiber or film*, USA Patent no.4551296, to Allied Corporation, 1985.

[44] F. H. J. Maurer, J. P. L. Pijpers, and P. Smith, *Process for the production of filaments with high tensile strength and modulus*, USA Patent no.4411854, to Stamicarbon B.V., 1983.

[45] S. Kavesh, and D. C. Prevorsek, *High tenacity, high modulus polyethylene and polypropylene fibers and intermediates therefore*, USA Patent no.4536536, to Allied Corporation, 1985.

[46] G. A. Harpell, S. Kavesh, I. Palley *et al.*, *Producing modified high performance polyolefin fiber*, USA Patent no.4455273, to Allied Corporation, 1984.

[47] T. P. Izod, M. B. Berenbaum, and M. H. Litt, *Method for removal of spinning solvent from spun fiber*, USA Patent no.5213745, to Allied-Signal Inc., 1993.

[48] J. A. P. M. Simmelink, R. Marissen, and V. Litvinov, *UHMWPE fibre and process for producing thereof*, USA Patent no.2010/0122517 A1, 2010.

[49] S. Kavesh, and D. C. Prevorsek, *High tenacity, high modulus polyethylene and polypropylene fibers and intermediates therefore*, USA Patent no.4413110, to Allied Corporation, 1983.

[50] P. Smith, and P. J. Lemstra, "Ultra-high-strength polyethylene filaments by solution spinning/drawing," *Journal of Material science*, vol. 15, no. 2, pp. 505-514, 1980.

[51] P. Smith, P. J. Lemstra, B. Kalb *et al.*, "Ultrahigh-Strength polyethylene fillaments by solution spinning and hot drawing," *Polymer Bulletin*, vol. 1, no. 11, pp. 733-736, 1979.

[52] Q. R. Zhu, K. L. Hong, L. Q. Ji *et al.*, "Morphological changes in annealed ultrahigh molecular weight polyethylene (UHMWPE) gel-films," *Journal of Polymer Science Part B: Polymer Physics*, vol. 33, no. 5, pp. 739-744, 1995.

[53] F. o. v. d. Cunha, A. k. d. nascimento, B. d. l. rue *et al.*, *Process for the preparation of polymer yarns from ultra high molecular weight homopolymers or copolymers, polymer yarns, molded polymer parts, and the use of polymer yarns*, USA Patent no.0290550 A1, to Braskem S.S, Profil Ind e com de fios ltda, 2008.

[54] J. Chen, X. Si, S. Hu *et al.*, "The Preparation and Study on Ultrahigh Molecular Weight Polypropylene Gel-spun Fibers," *Journal of Macromolecular Science, Part B*, vol. 47, no. 1, pp. 192-200, 2007.

[55] J. Smook, M. Flinterman, and A. J. Pennings, "Influence of spinning/hot drawing conditions on the tensile strength of porous high molecular weight polyethylene," *Polymer Bulletin*, vol. 2, no. 11, pp. 775-783, 1980.

[56] G. A. Harpell, S. Kavesh, I. Palley *et al.*, *Modified polyolefin fiber*, USA Patent no.4584347, to Allied Corporation, 1986.

[57] P. Hu, X. You, and Z. Liu, *Process for producing fiber of ultra high molecular weight polyethylene*, USA Patent no.2010/0233480 A1, 2010.

[58] T. Y.-T. Tam, Q. Zhou, J. A. Young *et al.*, *High tenacity polyethylene yarn*, USA Patent no.7,638,191 B2, to Honeywell International Inc, 2009.

[59] T. Y.-T. Tam, Q. Zhou, J. A. Young *et al.*, *High tenacity polyethylene yarn*, USA Patent no.7736561, to Honeywell International Inc., 2010.

[60] J. N. Magno, *Stretched polymers, products containing stretched polymers, and their methods of manufacture and examination*, USA Patent no.2009/0202801 A1, 2009.

[61] P. Smith, and P. J. Lemstra, "Ultrahigh-strength polyethylene filaments by solution spinning/drawing, 2. Influence of solvent on the drawability," *Macromolecular Chemistry and Physics,* vol. 180, no. 12, pp. 2983-2986, 1979.

[62] C. Sawatari, and M. Matsuo, "Morphological and mechanical properties of ultrahigh-molecular-weight polyethylene/low-molecular-weight polyethylene blend films produced by geletion/crystallization from solutions," *Polymer,* vol. 30, no. September, pp. 1603-1614, 1989.

[63] C. Sawatari, S. Shimogiri, and M. Matsuo, "Morphological properties of Ultrahigh Molecular Weight Polyethylene-Polypropylene blend films produced by gelation/crystallization from solutions," *Macromolecules,* vol. 20, no. 5, pp. 1033-1041, 1987.

[64] M. Matsuo, and R. S. Manley, "Ultradrawing at room temperature of High Molecular Weight Polyethylene," *Macromolecules,* vol. 15, no. 4, pp. 985-987, 1982.

[65] R. R. Marissen, E. F. Florimondus, E. F. F. D. De *et al.*, *Cut resistant yarn, A process for producing the yarn and products containing the yarn*, USA Patent no.2010/0050309, 2010.

[66] C. Anton, M. R. Mackley, and S. B. Solbi, "Extrusion processing of ultra-high molecular weight polyethylene; a new method for the production of high performance structures," *Polymer Bulletin,* vol. 17, no. 2, pp. 175-179, 1987.

[67] B. Kalb, and A. J. Pennings, "Spinning of high molecular weight polyethylene solution and subsequent drawing in a temperature gradient," *Polymer Bulletin,* vol. 1, no. 12, pp. 6, 1979.

[68] T. Kunugi, S. Oomori, and S. Mikami, "Preparation of ultra-high modulus polyethylene films by zone-annealing method," *Polymer,* vol. 29, no. May, pp. 814-820, 1988.

[69] T. Kunugi, A. Suzuki, and M. Hashimoto, "Preparation of high-modulus and high-strength poly(ethylene terephatalate) fiber by zone annealing," *Journal of Applied Polymer Science,* vol. 26, no. 1, pp. 213-221, 1981.

[70] T. Kunugi, C. Ichinose, and A. Suzuki, "Preparation of high-modulus and high-strength poly(ethylene terephthalate) film by zone-annealing method," *Journal of Applied Polymer Science,* vol. 31, no. 2, pp. 429-439, 1986.

[71] B. Kalb, and A. J. Pennings, "Hot drawing of porous high molecular weight polyethylene," *Polymer,* vol. 21, no. 1, pp. 3-4, 1980.

[72] B. Kalb, and A. J. Pennings, "Maximum strength and drawing mechanism of hot drawn high molecular weight polyethylene," *Journal of Materials Science,* vol. 15, no. 10, pp. 2584-2590, 1980.

[73] J. Smook, and A. J. Pennings, "The effect of temperature and deformation rate on the hot-drawing behavior of porous high molecular weight polyethylene fibers," *Journal of Applied Polymer Science,* vol. 27, no. 6, pp. 2209-2228, 1982.

[74] T. Y.-T. Tam, Q. Zhou, J. A. Young *et al.*, *High tenacity polyethylene yarn*, USA Patent no.7638191, to Honeywell International Inc., 2009.

[75] A. P. D. Boer, and A. J. Pennings, "Polyethylene networks crosslinked in solution: preparation, elastic behavior, and oriented crystallization. I. Crosslinking in solution," *Journal of Polymer Science,* vol. 14, no. 2, pp. 187-210, 1976.

[76] T. Ohta, Y. Ikeda, M. Kishimoto *et al.*, "The ultra-drawing behaviour of ultra-high-molecular-weight polypropylene in the gel-like spherulite press method:

influence of solution concentration," *Polymer,* vol. 39, no. 20, pp. 4793-4800, 1998.

[77] P. Smith, P. J. Lemstra, and H. C. Booij, "Ultradrawing of high-molecular-weight polyethylene cast from solution. II. Influence of initial polymer concentration," *Journal of Polymer Science: Polymer Physics Edition,* vol. 19, no. 5, pp. 877-888, 1981.

[78] M. Matsuo, and C. Sawatari, "Elastic modulus of polyethylene in the crystal chain direction as measured by X-ray Diffraction," *Macromolecules,* vol. 19, no. 7, pp. 2036-2040, 1986.

[79] M. Matsuo, C. Sawatari, M. Iida *et al.*, "Ultradrawing of High Molecular Weight Polyethylene Films Produced by Gelation/Crystallization from Solution: Effect of the Number of Entanglements," *Polymer Journal,* vol. 17, no. 11, pp. 1197-1208, 1985.

[80] T. Kanamoto, A. Tsuruta, K. Tanaka *et al.*, "On Ultra-High Tensile Modulus by Drawing Single Crystal Mats of High Molecular Weight Polyethylene," *Polymer Journal,* vol. 15, no. 4, pp. 327-329, 1983.

[81] K. Furuhata, T. Yokokawa, and K. Miyasaka, "Drawing of ultrahigh-molecular-weight polyethylene single-crystal mats," *Journal of Polymer Science: Polymer Physics Edition,* vol. 22, no. 1, pp. 133-138, 1984.

[82] T. Kanamoto, A. Tsuruta, K. Tanaka *et al.*, "Super-drawing of ultrahigh molecular weight polyethylene. 1. Effect of techniques on drawing of single crystal mats," *Macromolecules,* vol. 21, no. 2, pp. 470-477, 2012/08/14, 1988.

[83] I. Matheson Tri-Gas. 29 April, 2013; http://www.megs.ca/MSDS/Pdf/n-Hexane.PDF.

[84] J. Proctor, and M. Hughes, *Chemical hazards of the workplace,* 5 ed.: John Wiley and sons, Inc, 2004.

[85] I. sciencelab.com. 29 April, 2013; http://feql.wsu.edu/MSDS/dodecane.pdf.

[86] I. Sciencelab.com. 30 April 2013; http://www.sciencelab.com/msds.php?msdsId=9924436.

[87] A. f. T. S. a. D. Registry. 30 April 2013; http://www.atsdr.cdc.gov/toxprofiles/tp71-c2.pdf.

[88] S. c. Inc. 30 April, 2013; http://feql.wsu.edu/MSDS/dodecane.pdf.

[89] J. A. Dill, K. M. Lee, R. A. Renne *et al.*, "Î±2u-Globulin Nephropathy and Carcinogenicity following Exposure to Decalin (Decahydronaphthalene) in F344/N Rats," *Toxicological Sciences*, vol. 72, no. 2, pp. 223-234, April 1, 2003, 2003.

[90] F. Scientific. 30 April, 2013; http://fscimage.fishersci.com/msds/90868.htm.

[91] A. f. T. S. a. D. Registry. 30 April, 2013; http://www.atsdr.cdc.gov/ToxProfiles/tp113-c5.pdf.

[92] C. p. c. company. 30 April, 2013; http://www.cpchem.com/msds/100000014541_SDS_US_EN.PDF.

[93] U. s. d. o. labor. 30 April, 2013; http://www.osha.gov/SLTC/methylenechloride/.

[94] K. Foxall, "Toulene toxicology overview," H. p. a. UK, ed., 2007.

[95] V. Agarwal, "A study of the compatibility of polyvinylidene fluoride-hexafluoropropene and polyethylene as potential materials for dental floss," Heriot Watt University, 2006.

[96] M. A. Grompone, "sunflower oil," *Vegetable oils in food technology compositions,properties and uses*, F. gunstone, ed., Oxford: Blackwell Publishing 2011.

[97] A. Srivastava, and R. Prasad, "Triglycerides-based diesel fuels," *Renewable and Sustainable Energy Reviews*, vol. 4, no. 2, pp. 111-133, 2000.

[98] F. c. c. inc. "Orange terpenes", 1 April, 2013; http://www.sfm.state.or.us/cr2k_subdb/MSDS/ORANGE_TERPENES.PDF.

[99] M. F. Kemmere, M. W. A. Kuijpers, R. M. H. Prickaerts *et al.*, "A Novel Process for Ultrasound-Induced Radical Polymerization in CO2-Expanded Fluids," *Macromolecular Materials and Engineering*, vol. 290, no. 4, pp. 302-310, 2005.

[100] J. M. J. Paulusse, and R. P. Sijbesma, "Ultrasound in polymer chemistry: Revival of an established technique," *Journal of Polymer Science Part A: Polymer Chemistry*, vol. 44, no. 19, pp. 5445-5453, 2006.

[101] L. E. Scriven, "Physics and applications of dip coating and spin coating."

[102] M. E. Hall, "Coating of technical textiles," *Hand book of technical textiles*, A. R. Horrocks and S. C. Anand, eds., Cambridge: Woodhead publishing ltd, 2000.

[103] W. Fung, *Coated and laminated textiles*, Cambridge: Woodhead Publishing Ltd, 2002.

[104] Anonymous. "Thermal Analysis Tests", National Physical Laboratory, 22 June, 2012; http://www.materialssolutions.info/thermal.html.

[105] Anonymous. "Differential scanning calorimetry", Polymer Science Learning Center, The university of southern mississippi, 22 June, 2012; http://pslc.ws/macrog/dsc.htm.

[106] R. H. Lochner, and J. E. Matar, *Design for quality*, London: Chapman and Hall publisher 1990.

[107] C. Jones, "Field emission SEM training," *Hitachi S-4300 FE SEM*, H. W. University, ed., Hitachi High Technologies.

[108] W. E. Morton, and J. W. S. Hearle, *Physical properties of textile fibres*: The textile institute, 1993.

[109] H. de Vries, “A new approach to the continuum theory of birefringence of oriented polymers,” *Colloid & Polymer Science*, vol. 257, no. 3, pp. 226-238, 1979.

[110] L. Mascia, "Additives which assist processing," *The role of additives in plastics*: Edward Arnold, 1974.

[111] L. Mascia, *The role of additives in plastics*, London: Edward arnold publishers 1974.